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The Effects of Medium on the UV-Induced Photodegradation of Rhodamine B Dye

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ABSTRACT

This research seeks to compare the studies of Rhodamine B in various environments. Stemming from the author's interest in contemporary art sculptures, films made of transparent plastics were spin coated as model studies. The polymers chosen were polycarbonate (PC), poly (methyl methacrylate) (PMMA), polystyrene (PS), and polyvinylchloride (PVC), due to their availability to artists and known use in artworks for their physical properties such as flexibility. Industrially made, these polymers have a known timeline dictated for a society interested in the new objects in the market, rather than quality and well-crafted materials.

In order to understand the solid polymer environment's influence on Rhodamine B molecules, absorbance and fluorescence measurements were completed of Rhodamine B in solvents, in organic solutions with polymers, and in films cast of solutions. Interpretation was aided through the role of singlet oxygen and its vibrational dissipation onto and thus degradation of surrounding oxidizable species including solvents, polymers, and Rhodamine B dye molecules. Conclusions include the importance of solvent identity for Rhodamine B and polymer solution behavior, and the significance of polymer identity for film behavior. Important factors for fading rate of solutions include polymer: dye concentration and solvent identity, whereas degradation rate of films is dependent on polymer species and whether the film was annealed.

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CHAPTER 1. INTRODUCTION

1.1 MOTIVATIONS

Dyes and polymers are two organic materials combined in artworks. Dyes have been used through the centuries as a colorant to give artistic meaning to fiber arts and textiles. Fluorescent dyes utilize interactions with light to appear more saturated, brighter, and bolder when adsorbed or chemically bonded to a substrate. In modern art applications, plastic substrates have been dyed with these organic fluorescent molecules.[1]

In industry, Rhodamine B dye (RB) is termed basic violet 10. In contrast, plastics have a significant number of trade names due to their widespread distribution in modern society. Plastics used in modern art, such as those containing the polymers polycarbonate (PC), poly(methyl methacrylate) (PMMA), polystyrene (PS), and polyvinyl chloride (PVC) are applied to many types of everyday use, with an output of 100 million tons in the year 2000 across the world.[2] Artists create sculptures, installations, and multi-media paintings by exploiting these readily available, low-cost, colored plastics for their mechanical and optical properties.

1.2 Art Historical and Conservation Context

Since the beginning of the twentieth century, artists have strayed from the use of the traditional tools such as stone, clay, oil, canvas, watercolor, natural fibers, and wood. At this same point in history, scientists were discovering the macromolecular organics known as polymers. Modern art

movements, which redefined art styles through abstraction, included artists such as P. Picasso, M. Duchamp, and N. Gabo. These artists utilized innovative materials of the twentieth century to separate their artworks from the canonic traditions within art history. In the 1970s, artists such as F. Stella, A. Warhol, C. Accardi, and artists in the LA based Light and Space movement continued the divergence from traditional materials by creating artworks with fluorescent colorants in paintings, prints, and plastics. These artists chose plastics because of their interaction with light, and optical properties. These particular plastics demonstrate light transmission nearing 100% due to their chemically amorphous structure, meaning the molecules are oriented without order.

The major consequence of the stylistic and materialistic revolution in art was losing awareness of the reason for artistic traditions in materials − that reason being their longevity and stability. Through the centuries guilds compromised of artisans perfected the craft of oils combined with pigments on canvas or panel in Northern European countries, and the science of pigments in plaster, or dyes on fibers in countries such as Italy.[3] The introduction of modern materials to cultural heritage has proved to be a major issue in the field of art conservation.

Art conservation is a discipline aimed at the preservation of the materials of artworks with minimal invasion. Ethics plays a major role in choosing treatment options for chemical or physical problems, which detract

significance or legibility from artworks. There is sensitivity in the field toward any invasion that adversely may affect the historical object's future. In order to insure confidence in the protection of art objects, scientific examination will identify materials through non-destructive analysis, followed by testing conservation treatments on replicas, or studying chemical interactions of isolated materials in model studies.

This thesis research studied the isolated fading of RB dye in various model environments. This research will expand on environments in which RB photo-degradation has been studied, particularly those that mimic dyes impregnated in sheets of polymers, as used in modern and contemporary artworks. By redefining the application of RB fading, this study will probe chemical, physical, optical, and thermal interactions of RB with the most common polymers, in both the liquid and solid states.

1.3 STATE OF RESEARCH ON RB DEGRADATION

1.3.1 GENERAL RB PHOTOCHEMISTRY

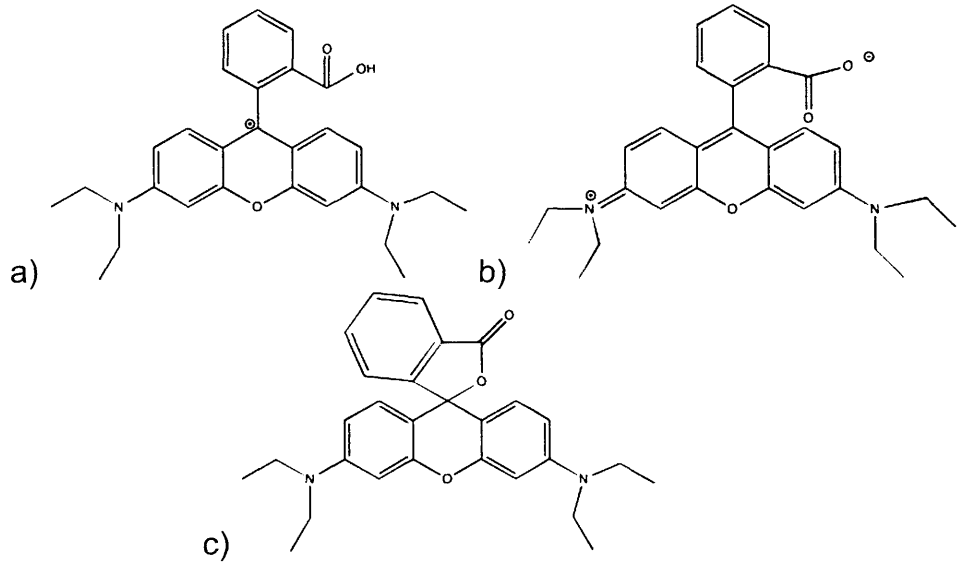

Figure 1: RB tautomers in equilibrium:
a) RB HR^+ b) RB zwitterion c) RB lactone

The three most major external influences on the chemical degradation of RB are heat, light, and humidity. As can be seen in Figure 1 of the chemical structure of the RB dye molecule in its various forms, the core xanthene structure serves as the chromophore. Due to the diethylamine group's structure on the chromophore, RB has more rotational freedom, and thus is more sensitive to temperature, than a comparative dye like rhodamine 101 with more rigid side-groups.[4] When heated, RB has more non-radiative options to dissipate energy absorbed, resulting in decreased fluorescence.

Although this paper will not analyze the fading of RB in the context of heat, since all experiments are done at room temperature, the thermal influence on the dye can be a contributing factor. Similarly significant is humidity, where the RB dye molecule is susceptible to hydrolysis reactions. The degradation studies in this work were completed at atmospheric humidity and in a well-ventilated hood, therefore, this discussion will not go into further chemical detail.

The main subject of this paper is the UV initiated photochemical reactions in RB molecules. The light stability of a dye molecule is influenced by both chemical and physical factors. The chemical influences include structural influences of electron donating or releasing groups, excited state susceptibility to a reaction, and environmental aspects like adjacent molecules, proximity to a light source, and incident radiative energy.[5] Physical factors including the dye molecule's size and concentration are important as well.

The chromophore of RB plays the most significant role in photochemical reactions. The concentration of the chromophore and substituents with electron donating groups, such as -OH, $-NR_2$, or $-O^-$ or electron withdrawing character, such as -COOH can be manipulated to change fading behavior in various types of environments. When dye molecules are concentrated enough ($M>10^{-5}$), they form covalent or non-covalent interactions between neighboring molecules, creating aggregates or

large clusters of molecules. Aggregates or dimers formed from RB have been shown to have slower kinetics in photodegradation.[6,7]

Basic photochemistry principles will be reviewed for the reader to understand the significance of excited state reactivity that is relevant to later discussions about RB. The Jablonski diagram illustrated in Figure 1 demonstrates the various electronic and vibrational states available to a molecule in a photochemical reaction. By absorbing energy, the chromophore in the ground singlet state (S_0) with paired spins becomes the excited state of S_1, where the spin is maintained, but where polarity, and thus solubility, of the molecule may change. The transition from the S_0 to the S_1 state is an electronic transition. In the figure, V.R. stands for the radiationless vibrational relaxation transition, which reflects the vibrational energy relaxation to the S_1 electronic level. Other electronic energy states in the diagram include S_0 or T_1. When a molecule reaches S_1, it has several subsequent options, which depend on the rate of the reaction being kinetically or thermodynamically prone. It can release energy in the form of radiation known as fluorescence, it can undergo a reaction that creates photoproducts with different structural features, or it can convert to a triplet state through intersystem crossing (I.S.C.).

I.S.C. is another radiationless transition, which is a forbidden by quantum mechanics, but still will occur from the lowest singlet state (S_1) to the energetically closest and lower in energy triplet state, T_1. When there is

enough time for an intermolecular interaction that releases a small enough energy to another molecule, I.S.C. occurs while also unpairing electron spins. When energy is released from the lowest triplet state, the radiative conversion is called phosphorescence; however, a radiationless transition that is spin-allowed would be from one molecule to another's triplet states.[8] The radiative emission of fluorescence has higher energy than the emission of phosphorescence, but the excited state of S_1 has a shorter lifetime than the excited state T_1.

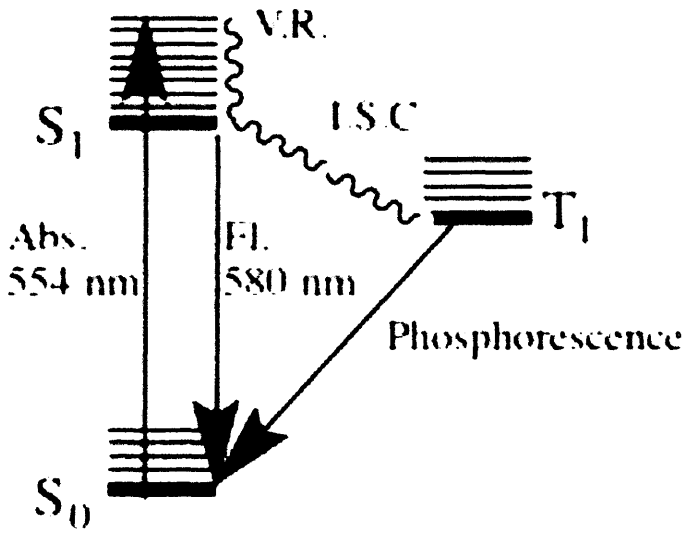

Figure 2: Jablonski Diagram illustrating basic photochemical Transitions of RB

The fluorescent dye of RB absorbs radiation at 554 nm, and emits fluorescence radiation at ~580 nm, particularly in a solution of RB in chloroform with 16 wt.% PMMA. As illustrated in the Jablonski diagram and by the principle of Stoke's Shift, the absorbance energy is higher than the

fluorescence energy. In the photochemical degradation of RB, the energy of absorption of the bonds is significant for the resulting reaction. When exposing RB to UV radiation from 360-370nm (320-330 kJ/mol) as done in this study, one can assume difficulty in cleaving bonds, except for C-C and C-0 bonds, which suggests the occurrence of small molecular weight, reactive photoproducts (see Table 1). The input of energy in C=C, N=N, or C=0 π bonds creates excited molecules that occur parallel to the molecular plane, where the electron charge distribution becomes more polarizable in the π* state.[10] More polarizable bonds reveals a potential change in solubility of excited RB-molecules compared to ground state RB-molecules.

Bond Type	Energy to Cleave (kJ/mol)
C-N	276
C=N	620
C-C	347
C=C	620
C-O	351
C=O	745
O-H	460

Table 1: Bond Energies relevant to RB

1.3.2 PHOTOCHEMICAL REACTIONS OF RB IN SOLUTIONS

The environment of RB plays a major role in the fading reaction mechanism. Xanthene dyes have intramolecular interactions based on their chemical environment that influence their distribution of electrons, switching between two constitutional isomers in the process known as tautomerism. A typical example of tautomer relationship is between the enol form and keto

form of two molecules. Although a subset of acid-base behavior, the phototropic species more thoroughly describe the relationship between HR^+, zwitterionic, and neutral leuco characters of RB, which range from colored pink to purple, to colorless (see Figure 1).[11] In a basic environment, the molecule will adopt its zwitterionic character through the deprotonation of the carboxylic acid group, and rearrangement of electrons to make a positively charged nitrogen atom. In contrast, a cationic form of RB exists in an acidic environment, where the sp^3-hybridized carbon is protonated. RB in solid form is usually purchased as a chloride salt, and is water-soluble.

The most significant photochemical reactions in this research involve photooxidation of RB, or N-dealkylation of the diethylamino groups, due to irreversible and permanent damage to the chromophore within the RB structure.[12,13,14] For the mechanism of photooxidation, there are both electronic intramolecular reactions, as well as intermolecular ones that must be considered for the two most involved species: RB and oxygen. The dye must be excited to its singlet state by absorption of energy, then releases energy through rotation of N-dialkylamine groups for a radiationless transfer of energy to relocate to the lower energy level, which is a longer-lived triplet state.[15] At this point, the triplet state of the dye is quenched either by colliding or reacting with another molecule, or if the dye is in high concentration and can form a dimer by hydrogen bonding between neighboring carboxylic acid groups.[16] A shift of charge is possible from the excited triplet state of the dye

to the triplet state of oxygen, which is the ground state of oxygen, due to the orbital distribution.[17] An interaction of one triplet with another is spin conversion allowed due to the same electronic spins, but only if the triplet donor had higher energy than the triplet acceptor.[18,19,20,21] On the other hand, RB is known for its fluorescence, rather than being particularly phosphorescent. A situation where an RB molecule was hindered from dissipating energy through radiationless pathways, and where the environment encouraged intersystem crossing of RB electrons to become unpaired would be necessary for the triplet-triplet transition of energy from RB to oxygen.

In comparison, the singlet states of RB and oxygen can interact, leading to formation of radicals, due to the excited singlet oxygen having two orbitals each with only one electron present. This orbital occupation reveals the possibility of radical formation through the acceptance or ejection of one electron while reacting with any other species in the environment, such as the singlet state of RB to form the radical cation.

1.3.3 PHOTOCHEMISTRY OF RB IN SUBSTRATES

A substrate can be defined as the medium within which a reaction occurs, or a surface, which absorbs the species of interest. In the context of this thesis, the substrate material is the solid polymer film, in which the photochemical reactions of RB take place. Both chemical and physical factors of a substrate are important to the photodegradation of the dyed material. A

chemical interaction that must be taken into account is the interaction of the substrate with singlet oxygen, thus resulting in oxidation of the substrate, causing more radicals in near proximity to the dye.[22]

Most of the chemical interactions between the dye and substrate are similar to those interactions between a dye and its solvent environment. However, the more significant discussion regarding the photochemistry of dyes in a substrate involves accounting for the physical aspects of the substrate, and for the lack of effects from the solvent. The ability for the substrate to protect the dye from external factors, such as temperature, oxygen, humidity, and UV light dictates the dye fading behavior.[23] If a dye is at the surface of the substrate, it is more prone to increased kinetic rates of photooxidation, photochlorination, or photoinduced N-dethylation of the diethylamino groups.

Intermolecular interactions between the dye and the substrate that are important to improving lightfastness include the concentration of the dye and thus its ability to form aggregates, the strength of the binding of the dye to the substrate, and the location of the dye within the substrate.[24]

Regarding the location of the dye, the porosity of the substrate is an important consideration, due to the ability of light, liquids, and gases to permeate through the surface to the more protected dyes.[25] The flexibility of the substrate dictates the ability for the dye to undergo conformational and translational movements, in order to maintain more stability and better

lightfast properties. In a more stiff, rigid, or crystalline material, a dye would have limited rotational or vibrational movement available, thus resulting in fewer radiationless transitions that could dissipate energy. A dye in a rigid substrate would theoretically be forced to undergo radiative transitions, such as fluorescence, instead of vibrating to dissipate energy onto a neighboring molecule. To a more extreme extent, the orientation of the dye plays a significant role in its ability to produce radicals and photodegrade, which was demonstrated with RB dyes in jelly-like materials.[26] Structural modifications of the dye or the substrate can affect the photochemical interactions, but this study did not aim for such minute comparisons, due to the attempt to understand the big picture of materials already being used to create artworks.

1.4. STATE OF RESEARCH ON POLYMER DEGRADATION

1.4.1 INTERNAL FACTORS

Although this thesis will not directly monitor the degradation of the polymer substrates in which RB will be embedded, there is a mutually destructive relationship between both materials due to their sensitivity to photooxidation.

To give a brief background, polymers are made up of a repeat unit structure called a monomer, to make long chain structures that can move around each other, or can become intertwined and cross-linked under specific conditions. There are three main types of polymers based on their thermal

properties - thermoplastic, thermosetting, and elastomers (rubber). Thermoplastics can be melted and reformed many times. In contrast, thermoset polymers can only be molded once, and if heated again, they will become charred. The polymers studied in this paper are all considered thermoplastics, but also viscoelastic, meaning they behave as elastic solids but also have a viscous flow like liquids.

Since different monomer structures react in varying synthesizing steps to form the polymer, the weaknesses in chemical structures can vary. The weakest link in the polymer chain can be identified as the initial source of degradation. The most likely reaction is dependent on the polymer's chemical and physical nature, as well as the surrounding environment. Bonds may break, redox reactions may occur, and molecules may crosslink, leading to ultimate degradation of the polymer.

Isotactic polypropylene (PP), low-density polyethylene (LDPE), and PS are called polyolefins, due to their waxy nature, and the polyolefin PS were studied in this work, since it absorbs UV radiation. Using Electron Spin Resonance (ESR), Faucitano and coworkers identified these polyolefins all having an oxidation mechanism involving radicals.[27,28] These free radicals that are photoinitiated in the polyolefins are detrimental if in the presence of RB dye, which begins fading by free radical initiation.[29]

Other polymers included in this study, such as PMMA and PC, contain bonds that absorb radiation in the UV region.[30] Further, the excited species of

these UV irradiated polymers are prone to react with atmospheric oxygen, thus shifting its energy to the O-O bond. This bond has energy of 145 kJ/mol (824nm), so there is thermodynamically favorable reallocation of energy from light particles. Once the oxygen is excited and photolysis occurs forming an oxygen radical, it reacts with an alkyl group forming hydro-peroxide, which is incredibly damaging to these polymers.

PC has a very strong UV absorbance, and thus in theory is predicted to degrade quickly by photooxidation.[31] The mechanism of PMMA photodegradation includes the photolysis of the ester group by radiation around 300-330 kJ/mol, forming tertiary carbon-centered chain radicals, alkoxy and acyl radicals.[27] These radicals initiate oxidative degradation propagated by peroxy and alkoxy radicals associated with the atmospheric oxygen.

Photooxidation of polymers, particularly in PVC, manifests in mechanical and physical properties such as a reduction in tensile strength, flexibility, and overall fragmentation of polymer chains due to the loss in molecular weight, even at temperatures as low as 50°C.[32] The degradation of dyes results in change of color through fading, but similarly oxidized polymers undergo yellowing.[32] Color is one of the earliest properties of polymers to degrade. The color changes can be monitored long before physical property damage appears, due to deprotonation, self-aggregation, or interaction with

other molecular or ionic species able to form molecular complexes like carbonyl groups.

Unlike the other polymers, PVC has a C-Cl bond, which absorbs light at 330 kJ/mol (362 nm). When PVC degrades, there is a buildup of polyenes in its backbone, causing discoloring. These polyenes are formed by the elimination reaction between the alkyl halide group and the alcoholic alkali, formed in the presence of a base. [33] When the carboxylic acid group on RB is deprotonated, the dye molecule serves as a base to encourage polyene buildup in the PVC polymer backbone. Further, the aromatic rings are oxidized by the same mechanism involved in the other polymers, causing mechanical and optical changes.

The physical state of the polymer plays a significant role in its photodegradation. In a study by Moadhen, RB was photooxidized and measured in porous silicon substrates.[34] The porous substrate allowed oxygen molecules to pass through to the dye, at a slower rate than if in solution,[17] and influenced energy transfer within the environment. Diffusion plays a key role in understanding the rate of light aging of dyes in polymer substrates, where larger porous spaces suggest the ability for larger aggregates to form, causing better lightfastness.[10]

1.4.2. EXTERNAL FACTORS

Factors that affect polymer degradation include the concentration of initiating species, type of radiation, excited states photochemistry, temperature,

moisture, and pollutants.[23] Although the temperature was kept constant at room temperature, it is important to note that thermal stability differs from photochemical stability of these polymers. In order, the least to most thermal stable polymers are PP, PE, PS, PVC, PC, and PMMA; the least to most stable photo-oxidative degrading polymers are PVC, PMMA, PE, PP, PS, and PC.[34]

Since the type of radiation and moisture were also controlled in this study, photochemistry of the excited state polymer could better be understood by the relationship with the initiating species. As has been proven through several papers, dyes act as photosensitizers to polymer degradation.[10,22,36] These photosensitizers transfer their elevated energy to atmospheric oxygen, which forms reactive singlet oxygen, causing photooxidative mechanisms reviewed above. There is a non-linear dependence of the rate of fading on the absorbance of the sample, which C. Giles asserted as he also refuted previous claims of this relationship being dependent on aggregation.[6] C. Giles has played a major role in elucidating the physical and chemical factors between RB and environments, such as polymer substrates; however, he never studied the exact combinations of RB with the polymers PC, PMMA, PS, and PVC.

1.5 GOALS AND OUTLINE

The purpose of this work is to monitor dye degradation through absorption and fluorescence spectroscopy to probe the influences of chemical and physical environments on RB fading initiated by UV light.

To reevaluate RB fading for the application of art materials, the dye was studied in the presence of four polymer solid substrates – PC, PMMA, PS, and PVC. A study was modeled with RB within simple solvent systems building to the complex solid substrates. First, RB was studied in organic solvents and potential photoproducts associated with spectral changes were identified. Next, polymers were added to the organic solvent solutions with RB, followed by the impregnation of RB into polymer substrates cast from the same organic solvents. These films were evaluated photochemically through RB, while the films were both annealed and unannealed. Finally, anisotropic fluorescence measurements were utilized to probe the mechanism of RB photodegradation in solid polymer substrates.

The innovation of this study is revealed through its reevaluation of the interaction between RB and its medium in its photodegradation. Other studies utilize the properties of RB for the sake of electronic, sensors, and laser applications, where this study seeks to exhaust the absorption and fluorescence studies for the application to RB dyes found within plastics.

CHAPTER 2. METHODOLOGY

2.1 MATERIALS

In order to isolate the materials in question and to simplify analysis, basic model systems were used.[10]

2.1.1 RB

Rhodamine B (479.02g/mol) was chosen due to its widespread use in art, electronics, and laser applications (see Figure 3). Further, the dye is soluble in aqueous and organic solvents giving the study a range of environments to study. In order to monitor the radiatiative transition of fluorescence in these systems, a molecule with a chromophore, which had strong and narrow fluorescence was needed. Rhodamine B is also a well-known dye used in industry for coloring plastics,[1] and is also used for the application of dye sensors, both of interest to this author due to overlapping research.

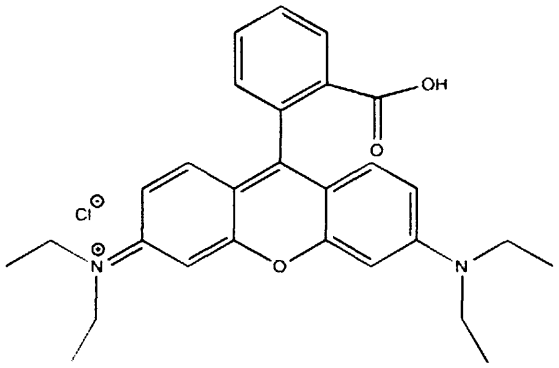

Figure 3: RB in salt form as purchased

2.1.2 SOLVENTS

Solvents were chosen based on their solubility compatibility with RB and polymers (see Figure 4).

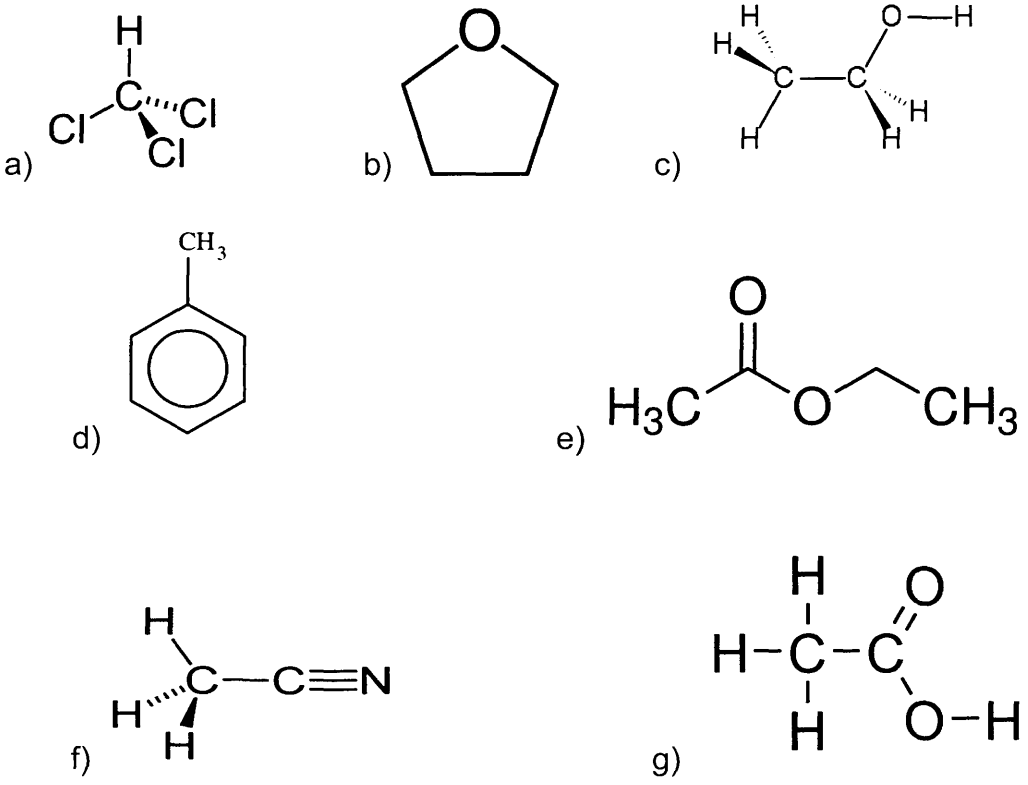

Figure 4: Solvents studied: a) Chloroform, b) Tetrahydrofuran (THF), c) Ethanol, d) Toluene, e) Ethyl Acetate, f) Acetonitrile, and g) Acetic acid

It was important for this study to have consistency with molar amounts of each material for comparative purposes. The literature has significant scholarship on RB in aqueous systems, and effect of pH on the fading

behavior, so this study chose to focus only on organic solvents.[19,37,38,39,40] Solubility tests were done on each solvent at 10mg/mL, 1 mg/mL, 0.1 mg/mL, and 0.01mg/mL. The concentration at which all the solvents chosen could solvate RB was 0.01mg/mL, so all stock solutions were made with this proportion. This small amount of RB helped avoid effects of aggregation during aging. Batches of 1 L solvent at 0.01 mg/mL were prepared and stored in cool environments and protected from light exposure. Due to varying densities of each solvent (see Table 2), it was important to calculate carefully to ensure constant molar amounts of RB in solution. The aim was to maintain $1.3 * 10^{-7}$ moles of RB in each 15 mL vial.

Solvent	Density (g/mL) at 25°C	Boiling Point (°C)
Chloroform	1.49	61
THF	0.889	65
Ethanol	0.789	79
Toluene	0.865	111
Ethyl Acetate	0.902	77
Acetonitrile	0.786	81
Acetic Acid	1.05	118

Table 2: Solvent Properties[40]

2.1.3 POLYMERS

All polymers were obtained from Acros Organics, pre-polymerized. The initial set of polymers varied from the final set due to solubility issues, where PE and PP both needed extensive sample prep to dissolve. Microwave technology was utilized to dissolve PE and PP in several solvents at 300 W

and for over 3 hours each. The protocol of making solutions involved adding a premixed solution of solvent with 10^{-7} moles RB (weight/volume ratio) directly to polymers in a vial, measured in respect to the weight of the overall solution weight. If the microwave method to dissolve PE and PP were used, it would expose RB to microwaves in solutions involving these semi-crystalline polymers, and thus would be an inconsistency across the data. Therefore, these polymers were eliminated from the study, despite their wide range of use in many applications. PMMA was purchased as beads in a 25 g container with an average M.W. of 25,000 g/mol. PC resin was purchased in pellet form in 5 g containers with an average M.W. of 45,000 g/mol. A 25 g container of PS was purchased with an average M.W. of 250,000 g/mol. Carboxylated PVC was bought with 1.8 wt. % carboxyl groups in a 100 g container with an average M.W. of 220,000 g/mol.

The polymer solutions were prepared in vials on a hot plate on low heat (~35°C), and alternating with sonication every 15-30 minutes until completely dissolved. Polymers (see Figure 5) were introduced at varying weight/weight (wt./wt.) percentages into RB-solvent solutions at 4%, 8%, 12%, 16%, and 20%. Polymer films were prepared from these polymer solutions by spin coating, and the annealed films were heated in a Fisher Scientific Isotemp Vacuum Oven, Model 282A above their glass transition temperature (T_g) for 16-20 hours for the polymer to achieve thermodynamic equilibrium.

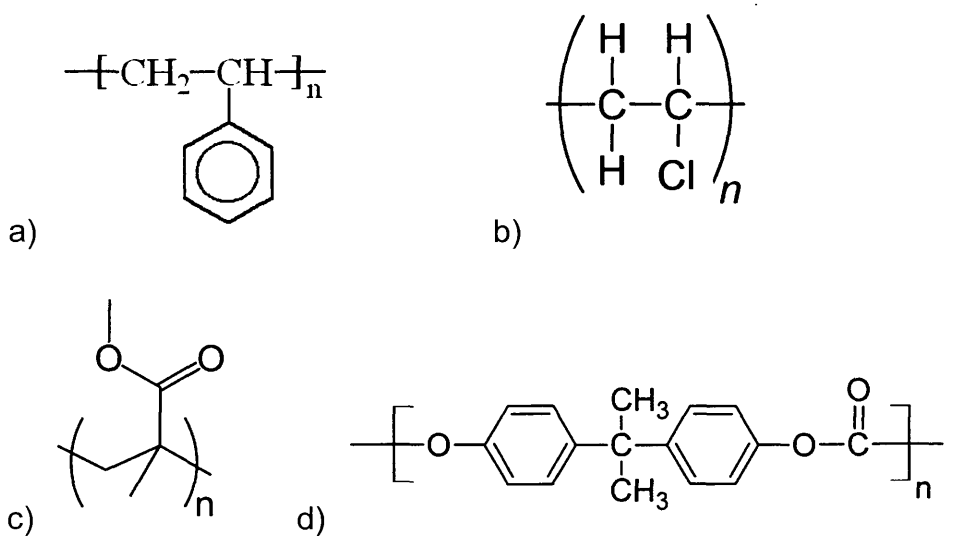

Figure 5: Polymer Chemical Structures: a) PS b) PVC c) PMMA d) PC

Polymer	T_g (°C)	δH [$MPa^{1/2}$]	Dielectric Constant
PS	97	19.26	2.5
PVC	80	19.5	3
PMMA	104	19.0	2.3
PC	145	20.43	2.8-3.4

Table 3: Polymer Properties for Solubility and Thermal Annealing

2.2 EXPERIMENTAL SETUP

2.2.1 SPIN COATING PROTOCOL

Microscope Cover Slip Slides (1" x 1") were cleaned by 20 minutes sonication in baths of (1) Acetone, (2) 10% NaOH, and (3) Deionized Water. Each slide was then dried with a Kim-wipe.

For spin coating, a CHEMMAT TECH Model KW4A, 110V instrument was used. The most ideal chuck for a smooth film was the 1.5" vacuum chuck with no grooves. For ease of removing the slide after spin coating with polymer, the chuck was pretreated with a thin layer of WD-40. The slide was then placed on the chuck, vacuum turned on, and settings adjusted. A glass pipette was filled to the start of the widest point with polymer-RB solution, before being dispensed a few millimeters above, and normal to the angle of the slide and chuck. After coated, the slide reverse was cleaned of excess polymer and WD-40 with acetone and a cotton swab before covering to protect from light before annealing. Instrumental settings were chosen based on the premise that the more viscous the solution, the faster and longer the instrument needed to be spun. For example, the viscous polystyrene at 12 wt.% in chloroform was set at 8,000 rpm for 18 seconds followed by 10,000 rpm for 60 seconds. A less viscous solution, like any PMMA concentration in any solvent was able to be spun at much slower speeds, like at 4,000 rpm for 18 seconds followed by 6,000 rpm for 60 seconds.

2.2.2 PROTOCOL FOR UV LAMP

A tungsten Dymax UV lamp powered by Light-Welder part #35137, which was borrowed from Professor Kranbuehl's lab was arranged exactly 23.7 cm above the samples. The UV light power was 3 mW at that distance, and the wavelengths emitted in the UV were 363 nm and 375 nm. The samples were always centered directly beneath the lamp, and a shield was

used to protect samples from any exterior light. The lamp was set up inside a fume hood with constant ventilation, in order to ensure constant temperature throughout the experiment, and in order to minimize temperature of irradiation through maximum airflow. The more time irradiated, the more degraded the sample became, as could be seen through the visualization of fading.

2.3 INSTRUMENTAL PROTOCOLS

2.3.1 UV-VIS MEASUREMENTS

A Cary 50 Bio UV-Visible Spectrophotometer instrument and software system was set for scanning wavelengths from 700 nm to 250 nm at fast speed. Baseline correction was utilized by blanking the system with a clean slide in the case of films, and with the appropriate solvent in the case of the solutions. Data was overlaid in the program, and auto-converted to ASCII (CSV) for analysis. When measuring films, a different sample holder had to be put into the instrument than the one used for measuring solutions in cuvettes.

2.3.2 Fluorescence Measurements

A Cary Eclipse Fluorescence Spectrophotometer instrument with accompanying software was set for scanning wavelengths from 540 nm to 700 nm. A manual scanning speed was set at 600 nm/minute, or 0.1 seconds/ 1nm scans. The excitation wavelength was set to 520 nm, and the slits varied depending on the sample. For brighter samples, smaller slits had to be used,

such as the combination of 2.5 nm excitation slit and 2.5 nm emission slit for PVC in chloroform. Larger slits needed to be used for fainter colored samples, such as 2.5 nm excitation slit and 10 nm emission slit for polystyrene in THF. Similar to the UV-VIS, this instrument needed to be fitted with a different sample holder attachment when collecting data from films instead of solutions.

2.3.3. GC-MS MEASUREMENTS

Initially, NMR was used to try to identify the photoproducts of RB; however, it was realized that NMR was not the appropriate technique when understood that there was a mixture of side products. In order to separate and identify RB photoproducts in solutions, GC-MS was utilized for its trace analytical detecting power. The departmental GC-MS was used, which was fitted with a non-polar column. After an initial run of a product, a messy spectrum revealed the need of using a derivatization agent in order to obtain a legible GC-spectrum. A silylation derivatizing agent, N,O-Bis(trimethylsilyl)trifluoroacetamide (BSTFA) was utilized to deactivate polar OH and NH groups. In Figure 6, the chemical structure of BSTFA is shown, and due to the strong electron-withdrawing group of CF_3, the bond between oxygen and silicon is weakened and will break.

Figure 6: BSTFA Chemical Structure

Experimental protocol needed to be exact and without impurities due to the strong analysis power of GC-MS. Chloroform solution was dried with sodium sulfate, before using in the RB solution. The 1.25 mg/mL 50 mL solution was irradiated with the UV lamp, and monitored with absorbance spectroscopy. After the solution was aged to the 50nm shift that represented the change in molecular species, the solution was rotovaped and put on the dry vacuum for ~6 hrs. A 3 mL amount of dried chloroform was added back to the dried RB product, and 1 µL was analyzed as a control with GC-MS. Chloroform pre-rotovaped and post-rotovaped were analyzed with GC-MS, as well as a chloroform solution of non-irradiated RB.

The ~3 mL solution of irradiated RB photoproduct was spiked with 100 µL BSTFA derivatizing agent, and heated to 60 °C for 30 minutes. Finally, 1 µL of spiked RB photoproduct was analyzed with GC-MS. A 6890N GC-system was paired with a 5973 MS for this analysis. Instrumental parameters included a spit mode at 51:101, and the front inlet was heated to 225 °C. A

nonpolar RXI-1MS column with 5 % methyl was used. The oven program included heating from 70 °C to 250 °C at a rate of 20 °C per min. In the MS detector, solvent delay was utilized, and masses from 35 to 550 m/z were detected.

2.3.4 FLUORESCENCE ANISOTROPY MEASUREMENTS

Fluorescence anisotropy was used as a tool to understand the movement of the RB molecules at the surface of the polymer films. An LS55 Perkin Elmer Fluorimeter was utilized. The application was run in single-read application mode, where only one excitation wavelength and one emission wavelength could be chosen for each anisotropic measurement. The slits were set at 10 nm excitation and 10 nm emission. The grating factor (GF) is unique for every instrument, and necessary for obtaining anisotropic values (r). The GF was measured with a depolarizing slide in order to correct for instrumental polarization. The value measured was 0.4545. The instrument needed to be fitted with its slide holder to measure the polymeric RB slides.

CHAPTER 3. RESULTS AND DISCUSSION

Many authors have attempted to elucidate the mechanism of RB photodegradation by studying RB's reactivity based on its immediate environment.[6,10,12,13,14,42,43] This section utilizes UV initiated degradation of RB paired with absorbance and fluorescence measurements to monitor photochemistry related to the color change in various mediums. The impetus of the study was for the application of art, and how RB responded to UV radiation in the solid phase of polymers. However, in order to understand the role of polymer in films, it was important to study the polymer in solutions first. In order for clarity of polymer influence compared to solvent influence, RB was first studied in the immediate environment of various organic solvents.

3.1.1 RB IN SOLVENT DATA

The chemical reactivity of RB was monitored through absorbance and fluorescence in the presence of several organic solvents, and one acid. The specific organic solvents were chosen in order to have a range of properties, such as their Hildebrand solubility parameter, dielectric constants, and various functional groups (see Table 4). Although the dielectric constants gave indications of electric charge within a molecule, solvents were also chosen for atomic or structural differences, such as the trihalide group in chloroform or the alkyl ring structure in THF.

Solvent	Hildebrand Solubility Parameter δH [$MPa^{1/2}$]	Dielectric Constant	bP (°C)
Toluene	18.3	2.38	111
Chloroform	18.7	4.81	61
THF	18.5	7.5	66
Ethyl Acetate	18.2	6.02	77
Acetonitrile	11.92	37.5	82
Ethanol	26.2	24.55	79
Acetic Acid	12.4	6.2	118

Table 4: More Solvent Properties: Within the highlighted solvents, RB undergoes major blue shift in absorbance upon UV irradiation

Stock solutions were made of ~10^{-7} moles RB with the same molar amount of each solvent. Smaller vials of ~15 mL were studied under UV irradiation. Comparing RB degradation in various solvents by both absorbance and fluorescence enabled the identification of three groups of behavior of RB in solvents: (1) very minor degradation (2) degradation and major hypsochromic shift (>45 nm), and (3) degradation with minor hypsochromic shift (≤10 nm). Group 1 included acetic acid, acetonitrile, and ethanol; group 2 included chloroform and THF; group 3 included ethyl acetate and toluene. Figure 7 shows representative absorbance spectra from each class. In the absorbance spectra, the shifts of group 2 can be traced further into the blue than with fluorescence spectra. Due to the nature of overlapping spectra between absorbance and fluorescence of a given fluorophore,

fluorescence is limited by the excitation wavelength, making major blue shifts difficult to distinguish from minor blue shifts.

Four major observations can be seen in this initial data: 1) there is an initial increase in absorbance before decrease in group 2 data, 2) there is a major blue shift in group 2 solvents, 3) there is not one solvent property that determines the classification to a particular solvent group, and 4) the time it takes for the absorbance of RB in groups 2 and 3 to be reduced to 50% of its maximum value at the λ_{max} is less than 30 minutes of UV irradiation. Looking at Table 5 data for chloroform and THF, even the decline in absorbance of RB in groups 2 and 3 solvents has reached 50%, the wavelength change has only proceeded ~30% of its total shift. This suggests that the fading of color proceeds faster than the change of wavelength.

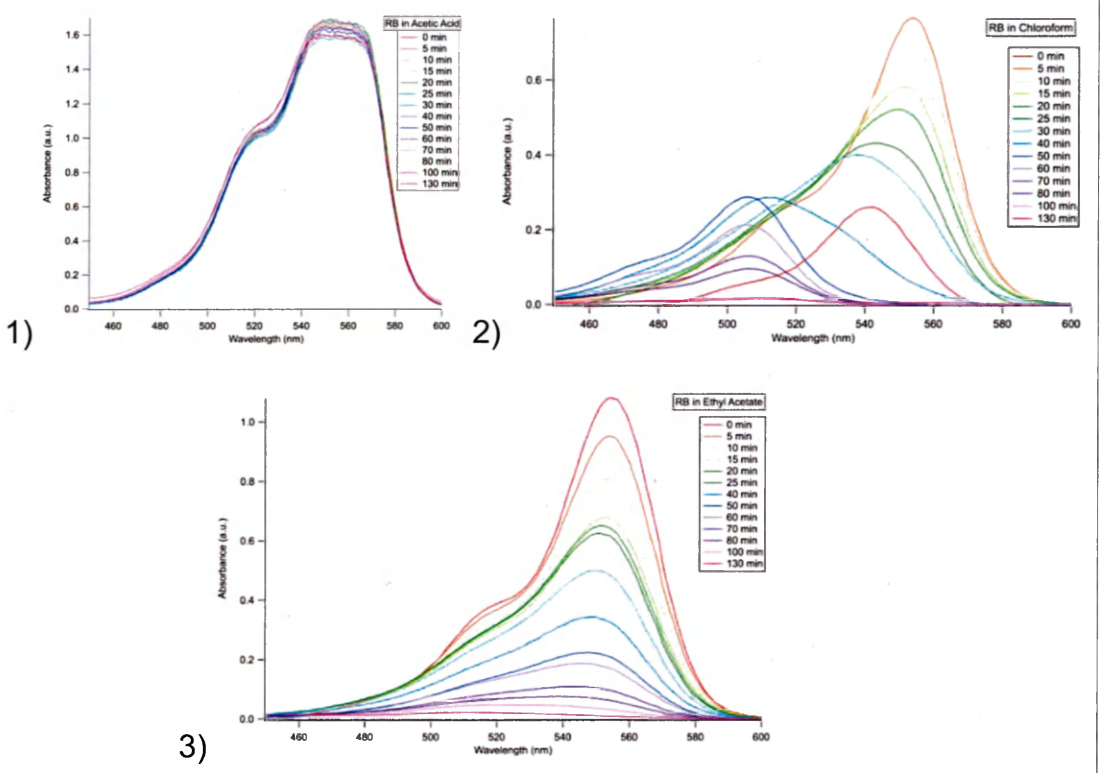

Figure 7: Absorption Classification of RB Groups 1, 2, and 3

Group	Solvent	Time to 50% max peak	Shift to 50% peak	Total Shift
1	Acetic Acid	-	-	-
1	Acetonitrile	-	-	-
2	Chloroform	≤30 min	553.00 nm → 537.95 nm	553.00 nm → 506.04 nm
1	Ethanol	-		
3	Ethyl Acetate	≤30 min		
3	Toluene	≤25 min		
2	THF	≤10 min	556.06 nm → 534.95 nm	556.06 nm → 498.02 nm

Table 5: Quantifying RB Solvent Trends through Absorption Data

Upon initial UV irradiation, the absorbance of RB in chloroform (group 2) actually increases (Figure 7). It continues to increase until irradiation time is 15 min, when it begins to decrease. This phenomenon also occurs in fluorescence data. Unlike fluorescence data, absorbance does not rely on any experimental parameters. Therefore, absorbance data suggests a change in molar absorbtivities of RB in group 2 solvents.

On the other hand, fluorescence spectra can be described through Figure 8. This figure shows the absorption and fluorescence being monitored to the left of their actual maxima, as pointed out by arrows excitation wavelength and emission wavelength. If there is a shift blue of decreasing wavelength, which occurs to RB in group 2 and 3 solvents to different extremes, the intensity will increase until hitting the maximum point. This realization brings to light that all λ_{max} values of all data may be off by a few nanometers to the blue, due to user error in settings. However, these settings were chosen due to their ability to capture the most precise data to encompass RB behavior in each of the chemical and physical environments studied.

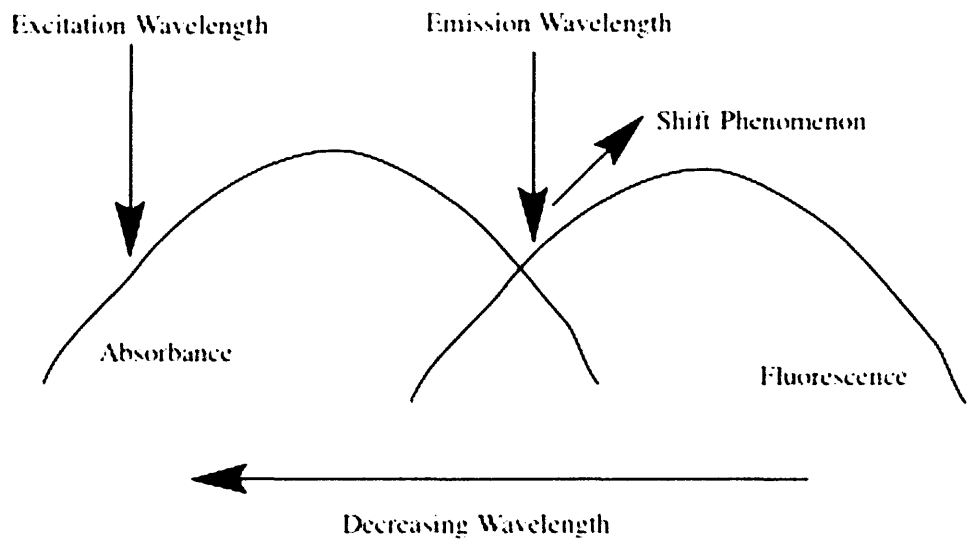

Figure 8: Shift Phenomenon of Increasing Intensity of RB curves

When comparing the degradation behavior of RB in chloroform and THF in the absorption and fluorescence spectra in Figure 9, it is clear that the absorption data represent the major shift of group 2 behavior more clearly. However, subtle variations between RB fading in THF compared to chloroform are easier to distinguish when viewing the fluorescence spectra. Fluorescence data are limited in displaying a blue shift, due to the basic overlap of the excitation spectrum with the emission spectrum, where the excitation source cuts off fluorescence data at a specific wavelength, while absorption does not compete with another light source. In both of these solvents, the absorption spectrum of RB reveals an initial increase in absorbance followed by a hypsochromic shift of approximately 50 nm while also fading. As shown in Table 5, RB in THF shifts to 498 nm, and RB in

chloroform shifts to 506 nm. Further, THF reaches half maximum absorbance in ~10 min, while chloroform takes ~30 min for the same decrease in absorption, which suggests that RB degradation processes are faster in THF than chloroform.

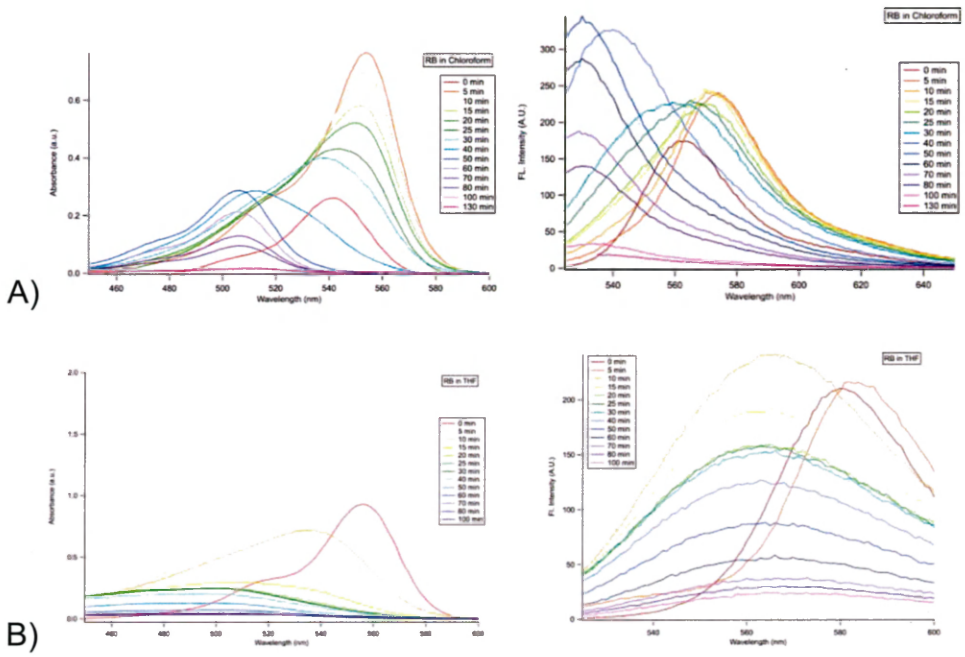

Figure 9: Absorption and Fluorescence RB Fading Group 2 Behavior. RB in A) Chloroform B) THF

According to Evans, the behavior of a major blue shift is due to change in chemical species from RB to several photoproducts. Evans concludes there are two photoproducts by the process of chlorination through electrophilic aromatic substitution while in the presence of chloroform[12] and three by the process of N-dealkylation in the presence of water.[13] With the

knowledge that RB forms photoproducts during the shift of RB in group 2 solvents, the initial increase in absorbance can be contextualized through the Beer-Lambert law, defined as: $A= (\varepsilon_s[s] + \varepsilon_P[P])\ b$. If the concentrations, and path length are kept constant, the only way for increased absorbance is through increased molar absorptivity of either the starting material, or the product being formed. Most likely this change is the result of the molar absorptivity of the photoproduct.

This author hoped to elucidate which type of photoproduct was formed when there was major blue shift in group 2 solvents. When exposed to UV wavelengths of light, N-dealkylation of the dialkylamine groups is a known photochemical reaction that occurs to other dyes.[12] In the case of RB this photochemical reaction produces photoproducts NN'-diethylrhodamine and NNN'-triethylrhodamine (see Figure 10).

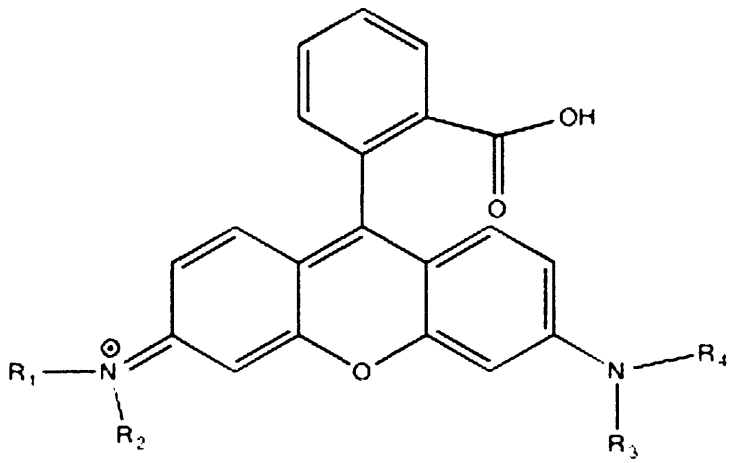

Figure 10: Photoproducts: NN'-diethylrhodamine, where $R_1 = R_3 =$ Ethyl, $R_2 = R_4 = H$, and NNN'-triethylrhodamine where $R_1 = R_2 = R_3 =$ Ethyl and $R_4 = H$.

GC-MS was used in an attempt to identify photoproducts in an irradiated solution of RB in chloroform. The sample was irradiated until the absorbance wavelength max shifted to ~509 nm. The technique of a derivatizing agent in GC-MS is used to isolate labile hydrogens, particularly those in RB, such as in the carboxylic acid group, and bonded to the sp^3-hybridized carbon at the top of the xanthene ring. The derivatizing agent was utilized in hope that small molecular weight photoproducts would become even more volatile when reacting with BSTFA, and thus evaporating and being isolated before further reacting within the GC to form more intricate side products.

GC-MS revealed the photoproduct ethoxytrimethylsilane, where the silane comes from the BSTFA derivatizing agent. This isolated photoproduct indicates oxygen de-ethylating a diamine group on RB (see Figure 11). In contrast, there was no chlorine species besides the pure solvent chloroform within the GC data of this sample, suggesting the chlorination mechanism had not occurred in this sample. Therefore, based on these absorbance measurements paired with GC-MS data, this author believes the shift to 509 nm to be the result of specifically the N-deethylation of the di-ethylamine groups of RB, in contrast to Evans' findings of chlorination combined with N-deethylation.

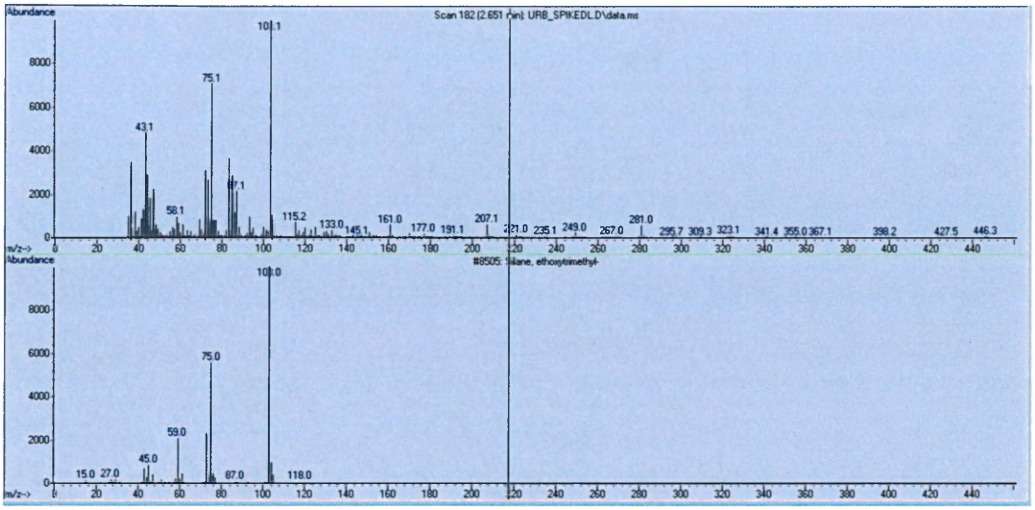

Figure 11: GC-MS data of ethoxytrimethylsilane matching analyte

Returning to the inability to explain chemically why RB exhibited different behavior in various solvents presented in Figure 7, the author considered the ability of some solvents to have higher concentrations than others of oxygen from the environment. According to the Handbook of Photochemistry, acetic acid, acetonitrile, and ethanol have the lowest concentrations of 9.04 mmol/L at 1 atm.[44] In comparison, the other solvents have an average of 10.5 mmol O_2 per liter solution, which brings to light the importance of examining photooxidation of RB.

The photooxidation of RB is a complex topic, due to the debate over the precise mechanism and main species involved in various environments. After significant debate, it is well known that singlet oxygen serves a role in the initial step of the degradation mechanism of an RB dye molecule.[17,18] Both

photophysical and photochemical studies have been done to test the type of oxygen of the mechanism, where photophysical methods include testing quantum yields and fluorescent lifetimes, and photochemical methods including setting up subsequent reactions that would proceed selectively by either singlet or triplet oxygen.[10,15,25,51] Studies have been extensive with many types of dyes, solutions, and substrates, but none of the literature has investigated RB with the solutions of organic solvents and polymers chosen in the next phase of this study.

To better understand the role of photooxidation of RB, an in depth discussion of the electronic interactions between RB and oxygen will follow. The orbital occupation of the ground level of triplet oxygen has two unpaired electrons in degenerate orbitals, creating a non-zero magnetic spin, classifying the species as paramagnetic. In comparison, the first excited state of oxygen is in the singlet state, where electrons are paired in one orbital, thus leaving an empty orbital for two electron reactions that are not accessible from the ground state. The triplet state of oxygen exhibits a strong electrophilic character, with energy of 22.5 kcal/mol. In comparison, the triplet state of the dye is at 43 kcal/mol, suggesting the thermodynamic ease of transfer from RB triplet state to oxygen triplet state.[50] The transfer of energy from RB triplet state to oxygen triplet state is one possible, yet a less probable interaction. This thesis study is not monitoring oxygen directly, but the role of oxygen can aid in the explanation of RB degradation in solution.

A 1972 study by D.R. Kearns investigated the effect of singlet oxygen on various solvents, and monitored the absorbance with the dye Methylene Blue.[45] In Kearns' study, it was expected that singlet oxygen lifetimes would be very long in solvents that contained nitrogen, and theoretically the longest in chloroform as a solvent. Kearns' experimental data did not agree with his computational predictions that chloroform would have the longest singlet oxygen lifetime. Similar to Kearns' experimental data, when the dye was photodegraded in chloroform it did not have a noticeably slow fading process; whereas, as seen in Figure 12, acetonitrile, acetic acid, and ethanol had the slowest rates compared to the other organic solvents. Further, the data collected in this thesis reveal a major shift and degradation of RB when in chloroform, suggesting inaccuracy in Kearn's prediction of oxygen lifetimes in chloroform, and that singlet oxygen promotes stability, rather than fading of RB.

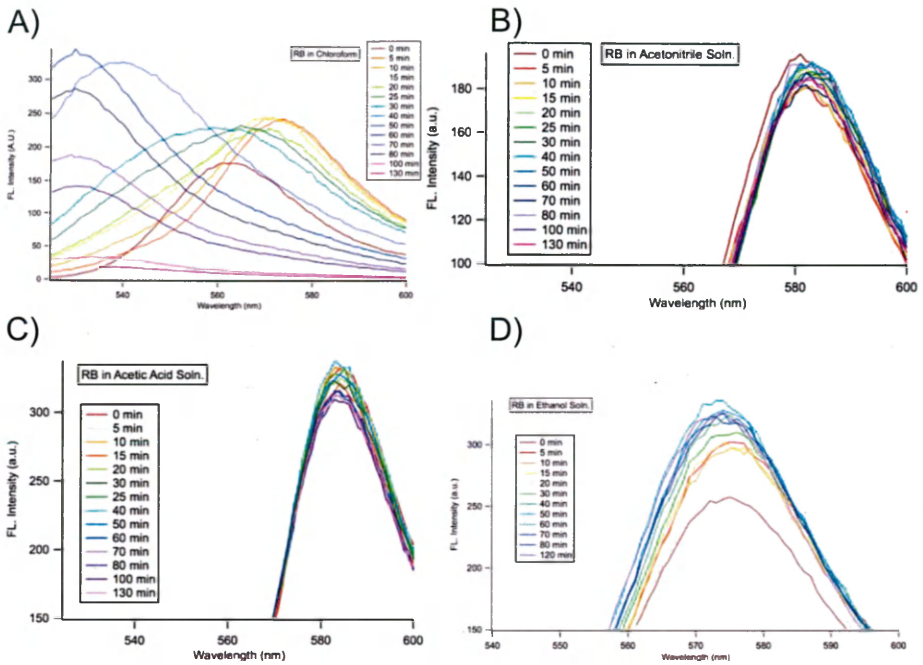

Figure 12: Fluorescence Fading Comparison: RB is in A) Chloroform, B) Acetonitrile, C) Acetic Acid, and D) Ethanol.

As revealed in a study aimed at understanding the decay of singlet oxygen in various solutions undertaken by P.B. Merkel, it was suggested that radiationless transfer from oxygen to solvent in the form of vibrations was significant for the dissipation of energy. Specifically, Merkel suggested tracing a strong infrared absorption of the solvent at 7880 and 6280 cm^{-1}, where large amounts of electronic energy from singlet oxygen can be turned into vibrational excitation of the solvent.[50] The first vibrational energy represents the value obtained if singlet oxygen transferred all its excitation energy, and the second represents the amount of excitation energy that would be released from the ground electronic state of singlet oxygen. If singlet oxygen is

transferring energy to the solvent, then it would not be transferring that energy to the dye, and would result in increased lightfastness. This trend observed by Merkel reveals that in solvents with nitrogen or argon, which do not absorb in the infrared the singlet oxygen should have the longest lifetime, thus supporting the data of RB fading in acetonitrile.

To delve further into how singlet oxygen lifetime affects RB fading, a study by Adams and group explain that triplet energy transfer from many of the sensitizers to an oxidizable species is possible.[9] In their paper, the oxidant was considered of negligible importance due to the relative concentration of oxygen being 30 times that of the oxidant. However, there must be a concentration at which the oxidizable species would be excited, and the sensitizer would transfer its energy to this species, in turn degrading it.

According to the reaction rates determined in Adams' study of the same phenomenon, the concentration of oxygen is a contributing factor to the rate of reaction involving an oxidizable species. In Figure 13 steps 1 and 2b, one can see that a sensitizer species, which can attain its triplet state through exposure to a certain wavelength of light, will transfer its energy to the triplet state of oxygen, which RB can do. In step 3a, the singlet oxygen formed by reaction of the sensitizer with light goes on to oxidize an oxidizable species. Looking at the mechanism and related rate laws of reactions, one can conclude that in solvent solutions with RB, the dye serves as the sensitizer,

and M is any material that protects RB from becoming the oxidant. If a species M, like a solvent or polymer is being oxidized, RB molecules are not, and are maintaining color. According to Kearns, solvent polarizability, ionization potential, oxygen solubility, and viscosity are irrelevant to the radiationless decay of singlet oxygen, but the solvent character does seem significant when the small molecule oxygen transfers electronic energy into vibrational excitation of the solvent.[45]

Reaction	Rate
1) $S + h\nu \rightarrow {}^1S^* \rightarrow {}^3S^*$	$I_a\Phi_T$
2) ${}^3S^* \rightarrow {}^1S$	$k_1[{}^3S^*]$
2a) ${}^3S^* + {}^1M \rightarrow {}^3M^* + {}^1S$	$k_1[{}^3S^*][{}^1M]$
2b) ${}^3S^* + {}^3O_2 \rightarrow {}^1O_2^* + {}^1S$	$k_1[{}^3S^*][{}^3O_2]$
3) ${}^1O_2^* \rightarrow {}^3O_2$	$k_2[{}^1O_2^*]$
3a) ${}^1O_2^* + M \rightarrow MO_2$	$k_2[{}^1O_2^*][M]$

Figure 13: Adams' RB Photo-degradation Mechanism & Rate Laws. S is a sensitizing agent, I_a is rate of absorption of photons by sensitizer, Φ_T is the quantum yield of production of triplet sensitizer in the presence of oxygen, and M is the oxidized species. * denotes an excited state.

RB-in-solvent data provided several conclusions important to future studies. Degradation processes in group 2 solvents may have similar spectral characteristics; however, RB degradation processes are faster in THF than chloroform. Also, the fading of color proceeds faster than the change of

wavelength in RB in these solvents. Lastly, singlet oxygen lifetimes have an indirect correlation with lightfastness of RB.

This thesis hypothesizes that the ability of the medium of the dye to obstruct or to aid the interaction of specific orbital states of RB and oxygen predict the fading mechanism, kinetics, and photoproducts. This ability for the dye to restabilize and equilibrate itself after UV irradiation through movement may be less possible when surrounded by larger polymeric molecules.

3.1.2 RB AND POLYMERS IN SOLVENT DATA

Due to this author's interest in contemporary art made of dyed plastics, the effects on RB degradation was questioned in the context of the Adams oxidative mechanism (see Figure 13). Assuming that both RB and polymer can act as an oxidizable species (M) in the above mechanism by Adams, three questions arose: 1) will the degradation rate change as a function of the polymer concentration, 2) how does the degradation rate change in presence of different polymers, 3) will the polymer identity change the solvent group classification. All these questions were further investigated through absorbance and fluorescence measurements.

UV degradation of a constant concentration of RB was studied through absorbance and fluorescence in solutions with increasing concentrations of 4 wt.%, 8 wt.%, 16 wt.%, and 20 wt.% PMMA in chloroform (see Figure 14).

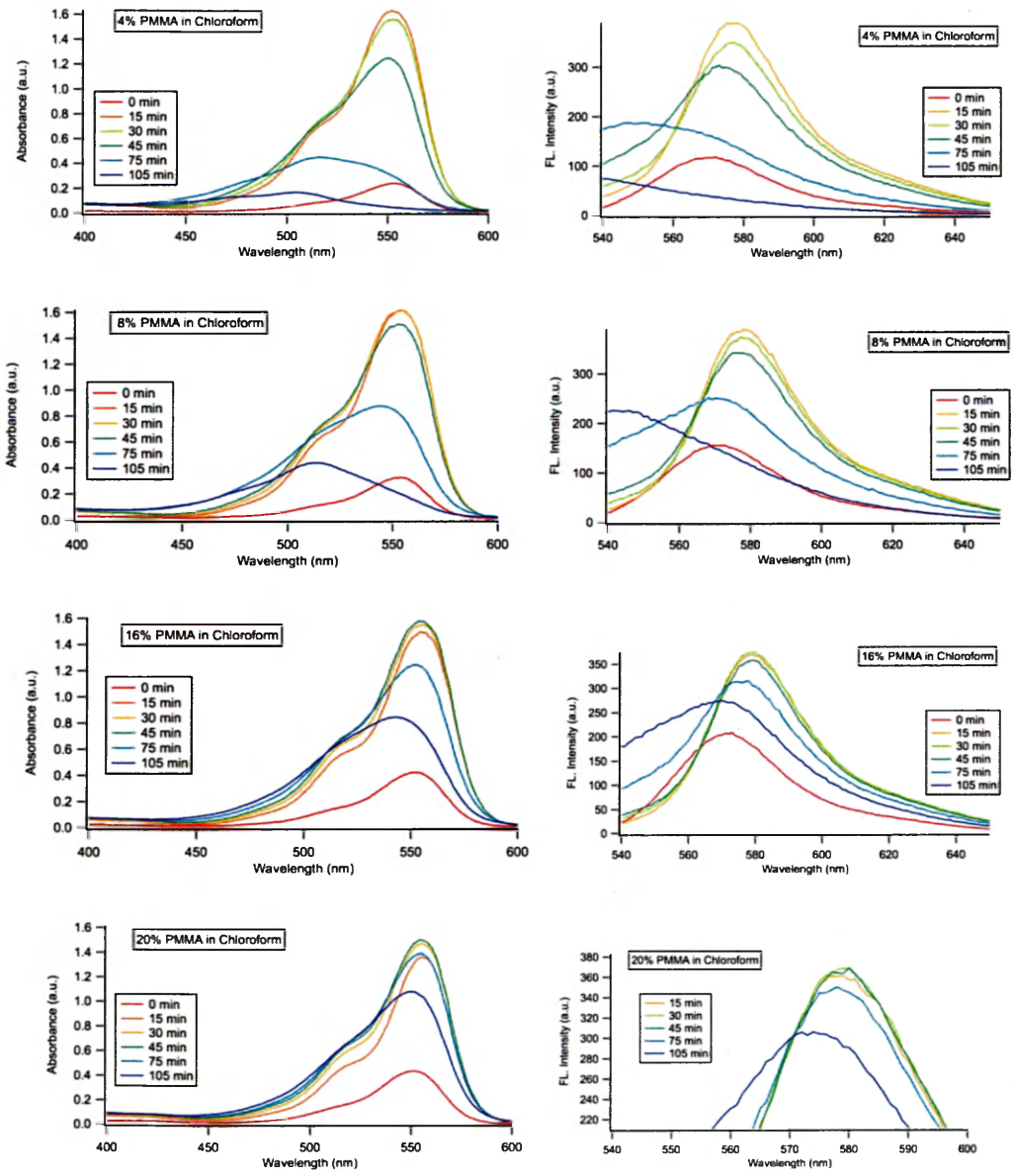

Figure 14: Absorbance and Fluorescence trends of RB-chloroform solution with varying polymer wt. %

These graphs in Figure 14 show that as the polymer concentration increases, the magnitude of the blue shift becomes smaller in both

absorbance and fluorescence. With more polymer in the solution, less RB fading is apparent, suggesting that UV degradation has more options of types of molecules to degrade, since both species can be oxidized.

Further, these graphs visually demonstrate the ability to use absorbance, rather than fluorescence to distinguish between lower and higher wt.% of polymer. Quantitatively depicted in Table 6 of RB in chloroform with 4 wt.% PC, there is a fluorescence $\Delta\lambda$ shift from 577 nm → <540 nm, where absorbance shows exactly 552 nm → 576 nm. In data of 16 wt.% PC in RB-chloroform solutions, a fluorescence $\Delta\lambda$ shift of 577.05 nm → 548.05 nm, and an absorbance $\Delta\lambda$ shift of 555.04 nm → 516.93 nm.

Although the Figure 14 data show only PMMA in chloroform, they are visually representative of the trend of all polymers in all solutions to have a shift with less magnitude as the polymer concentration is increased. Quantitatively, the last column in Table 9 reveals RB in chloroform with 4 wt.% PMMA has a blue shift of 36.93 nm within the first 75 minutes. In comparison, 20 wt.% PMMA in a RB-chloroform solution has a red shift of 4.04.

In order to continue to compare qualitatively and quantitatively the wavelength shifts and fluorescence intensity fading across all combinations of polymers and solutions, data were collected and normalized within Tables 6-9. The calculation, which represents the gradient of change within a certain amount of time was done using the percentage of change in fluorescence

intensity (ΔI). This value was calculated by recording the maximum and minimum intensity data of the spectra at 572.05 nm and between 0 min and 45 min. Then the fluorescence ΔI (%) is defined as:

$$\left(\frac{\qquad\qquad}{\qquad\qquad}\right) \times 100$$

For example, the ΔI value of 56.8 % in Table 9 of RB-chloroform solution with 4 wt.% PMMA reveals major RB fading. In contrast, the value of 6.0 % in Table 8 of RB-THF solution with 12 wt.% PVC is very minor fading. Some data show large amounts of change in fluorescence from the maximum spectra to the minimum spectra, but the change represents the inverse of fading, that is, brightening. An example of increasing color intensity is the large value of 98.8% in Table 6 of RB-THF solution with 8 wt.% PC. This data set can be interpreted as a much slower evolution in degradation, where RB will hit a maximum, and eventually degrade and decrease intensity.

When comparing RB fluorescence ΔI values with 4 wt.% polymer in solution, some trends emerge showing how degradation rate varies based on the addition of different types of polymers in solutions. RB solutions at 4 wt.% PC has the most drastic ΔI values in both chloroform and THF at 95.8% and 98.8%, which follows logic since RB in these solvents shows the most drastic Δλ shift (see Table 6). However, these values give contrasting results. In the chloroform solution, RB in 4 wt.% PC degrades rapidly and drastically, but while in THF solution, RB in 4 wt.% PC does not fade, and only fluoresces brighter. This suggests that the most extreme behavior of degrading and the

most extreme behavior of stability are both present both in PC data. Within one polymer type of PC, RB degradation rates can be on both ends of the spectrum. This trend of a polymer within the RB solutions of chloroform and THF having contrasting behavior also appears with 4 wt.% PMMA. If solubility issues were not a problem, this comparison could be made with solutions of PS and PVC. With the data collected, it can be concluded that RB in THF shows slower fading kinetics compared to chloroform.

Solution Composition	Fluorescence ΔI (%) up to 45 min	Fluorescence Δλ up to 75 min	Absorbance Δλ up to 75 min
RB in Chloroform with 4 wt.% PC	95.8	576.02 nm → <540nm	552.95 nm→ 501nm
RB in Chloroform with 8 wt.% PC	88.0	577.05 nm→ 544.02 nm	553.99 nm → 511.05
RB in Chloroform with 12 wt.% PC	77.2	576.02 nm → 548.05 nm	552.99 nm → 522.98 nm
RB in Chloroform with 16 wt.% PC	85.0	577.05 nm → 548.05 nm	555.04 nm → 516.93 nm
RB in THF with 4 wt.% PC	Overall increase (96.0)	576.02 → 570 nm	No shift
RB in THF with 8 wt.% PC	Overall increase (98.8)	576.02 nm → 568.95 nm	No shift

Table 6: Quantitative Data for PC solutions

Solution Composition	Fluorescence ΔI (%) up to 45 min	Fluorescence Δλ up to 75 min	Absorbance Δλ up to 75 min
RB in Chloroform with 4 wt.% PS	18.6	No shift	Increased intensity- no shift
RB in Chloroform with 8 wt.% PS	12.8	572.94 nm → 577.94 nm	Increased intensity- no shift
RB in Chloroform with 12 wt.% PS	23.1	575.00 nm → 581.01 nm	Increased intensity- no shift
RB in Chloroform with 16 wt.% PS	17.5	572.05 nm → 577.05 nm	Increased intensity- no shift
RB in Chloroform with 20 wt.% PS	15.7	572.95 nm → 577.94 nm	Increased intensity- no shift

Table 7: Quantitative Data for PS solutions

Solution Composition	Fluorescence ΔI (%) up to 45 min	Fluorescence Δλ up to 75 min	Absorbance Δλ up to 75 min
RB in THF with 4 wt.% PVC	24.8	583.04 nm → 567.01 nm	553.99 nm → 514.06 nm
RB in THF with 8 wt.% PVC	17.0	583.04 nm → 575.00 nm	552.95 nm → 516.93 nm
RB in THF with 12 wt.% PVC	6.4	582.02 nm → 576.02 nm	555.98 nm → 551.95 nm

Table 8: Quantitative Data for PVC solutions

Solution Composition	Fluorescence ΔI (%) up to 45 min	Fluorescence Δλ up to 75 min	Absorbance Δλ up to 75 min
RB in Chloroform with 4 wt.% PMMA	56.8	577.94 nm → <540nm	552.95 nm → 516.02 nm
RB in Chloroform with 8 wt.% PMMA	29.9	577.94 nm → 541.04 nm	552.95 nm → 542.02 nm
RB in Chloroform with 12 wt.% PMMA	14.6	578.97 nm → 575.00 nm	551.95 nm → 554.04 nm followed by shift blue
RB in Chloroform with 16 wt.% PMMA	(5.6)	580.00 nm → 577.94 nm	552.95 nm → 552.05 nm
RB in Chloroform with 20 wt.% PMMA	3.0	580.00 nm → 577.94 nm	551.00 nm → 555.04 nm
RB in THF with 4 wt.% PMMA	Overall increase	Maxed out at same settings	556.98 nm → 493.06
RB in THF with 8 wt.% PMMA	Overall increase	Maxed out same settings	555.93 nm → 493.06 nm
RB in THF with 12 wt.% PMMA	Overall increase	584.05 nm → 541.94 nm	554.04 nm → 488.07 nm
RB in THF with 16 wt.% PMMA	Overall increase	572.05 nm → 557.94 nm	555.93 nm → 497.00 nm
RB in THF with 20 wt.% PMMA	Overall increase	572.05 nm → 556.02 nm	551.00 nm → 497.00 nm

Table 9: Quantitative Data for PMMA solutions

Fluorescence may be limited, like in the Δλ shift of ≥37.94 nm in the sample of RB in Chloroform at 4 wt.% PMMA in Table 9, but the absorbance

data give an exact picture of the shift of 35.98 nm. In comparison, when there is a minor shift red of 4.99 nm in fluorescence, there is not necessarily a shift evident in absorbance data, as can be seen in Table 7 with 20 wt.% PS in RB-chloroform solution with no shift in absorbance.

Where fluorescence is showing a minor change through a blue spectral shift, the corresponding absorbance data reveal another interpretation. Absorbance data show that the degradation in RB-chloroform solutions in PC have still not yet taken place, and RB has higher absorbance, or increasing molar absorptivity. The complementary fluorescence data reveal minimal change of intensity. Although RB has increasing absorbance, its fluorescence degradation does not correlate, suggesting the role of the polymer in dissipation of some of the absorbed energy without harming RB. Despite this outlier, a small value in fluorescence intensity cannot be accepted as a sign for lack of RB degradation, as can be seen by looking at Table 8. This chart quantifies the fading and shifting within RB-THF solutions with PVC. In the case of 4 wt.% PVC in RB-THF solution, the fluorescence ΔI value of 24% suggests some, but not significant fading. The absorption data reveal a major blue shift of almost 40 nm, revealing the importance of using both absorption and fluorescence data to interpret the environmental influence of polymers and solutions on the degradation rate of RB.

In the previous section on RB degradation behavior in solvents, three groups of behavior were identified for how the dye responds within certain

solvents. This trend continues to be obvious in most cases like 4 wt.% PC in a RB-chloroform solution, but is complicated by the presence of the polymer in others, like 20 wt.% PS in a RB- chloroform solution, or 4 wt.% PVC in a RB-THF solution. One of the main issues at this point was solubility, and the inability to dissolve some of the polymers in the solutions (see Table 10). In order to report data from groups 2 and 3 without major solubility issues, chloroform, THF, and ethyl acetate were chosen as the main solvents to study.

Group	Solvent	PS	PC	PMMA	PVC
3	Toluene	Yes	No	Yes	Yes
2	Chloroform	Yes	Yes	Yes	Partially
2	THF	Partially	Partially	Yes	Partially
3	Ethyl Acetate	Partially	No	Yes	Partially
1	Acetonitrile	No	No	No	No
1	Ethanol	Yes	No	No	No
1	Acetic Acid	Partially	No	No	Yes

Table 10: Solubility of Polymers in Solvents

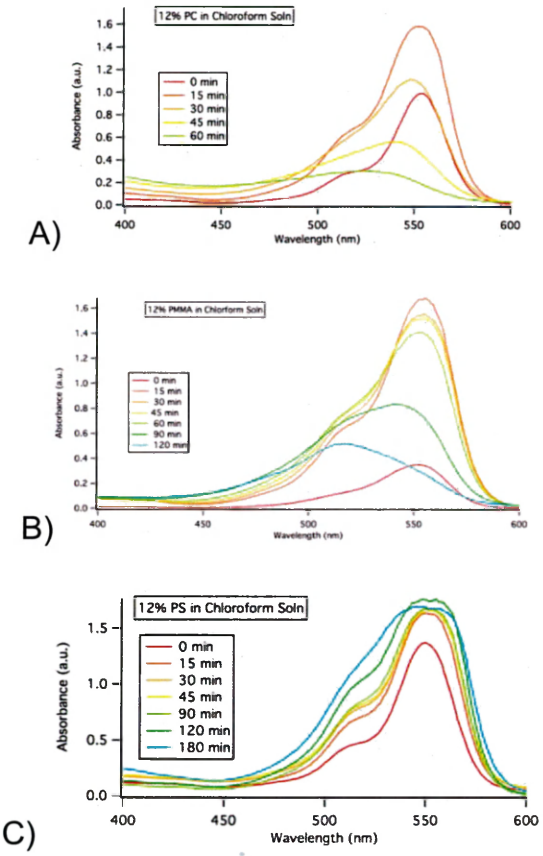

Figure 15: RB-Chloroform Solution Comparison with 12 wt.% Polymers: Comparing Fading Times in Group 2, where A) PC, B) PMMA, and C) PS

Here, several fluorescence spectra will be used to interpret the role of polymer identity on solvent classification. When looking at data of 12 wt.% polymers with the same concentration of RB in chloroform, RB degrades quickest in the presence of PC, and in PS appears to be increasing in absorbance. These data suggest that PC degrades more readily, and PS

least readily than the other polymers when in the presence of chloroform (see Figure 15). The behavior here of RB in chloroform with polymers remains according to solvent assigned group 2 classification.

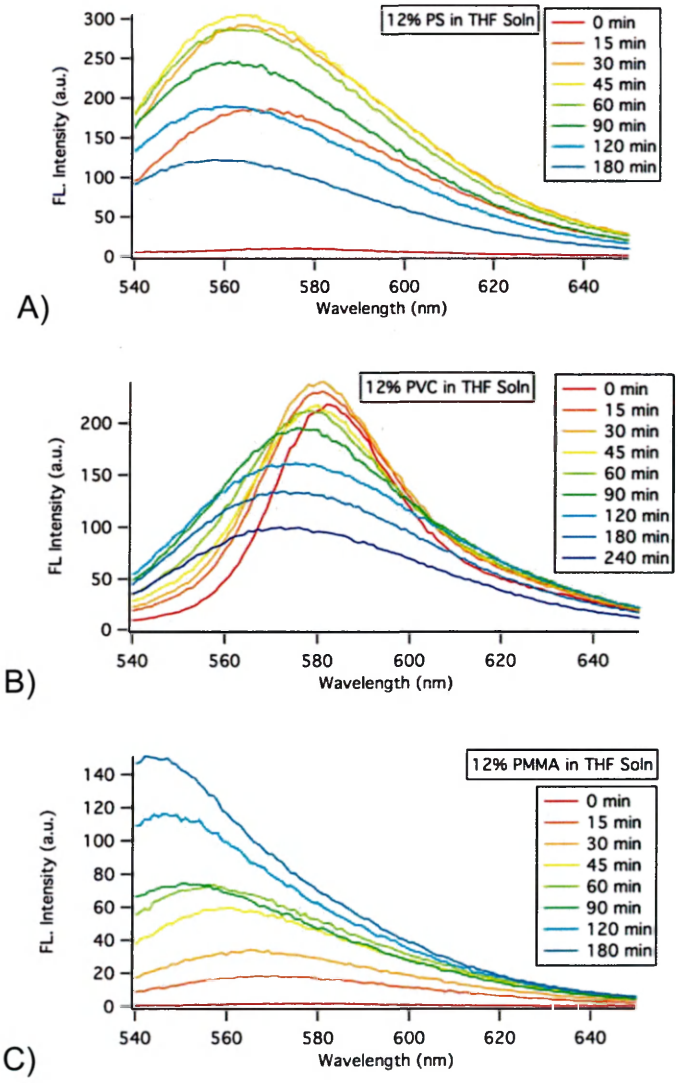

Figure 16: Comparison of RB-THF solutions with 12 wt.% polymers- A) PS, B) PVC, C) PMMA, D) PC

Fluorescence spectra show smaller variations due to polymer identity that result in changes of solvent classification. Particularly, group 2 behavior is not maintained when polymers are added to solutions of RB in THF. When PS and PVC are introduced separately at 12 wt.%, the shift in RB degradation is obvious due to the marked behavior of an initial increase of fluorescence intensity before a decrease around 35- 60 min (see Figure 16). In a RB-THF solution accompanied by PS molecules the spectrum is broadened during the entire kinetics experiment suggesting more RB molecules undergoing degradation, thus giving a less distinct intensity peak. RB in THF surrounded by PVC shows a more characteristic slow broadening of the RB fluorescence spectrum as it degrades. In contrast, RB in THF with PMMA acts very differently: a steady increase from almost no fluorescence intensity to the intensity of ~150, and accompanied by a major blue shift.

If the intensity of RB only increases in THF with PMMA, it suggests that the kinetics of RB degradation have slowed down. The role of PMMA in the RB-THF solution may be quenching singlet oxygen, and also may not be giving off many radicals that would react further with RB. This argument would agree with knowledge that PMMA is one of the most stable polymers of this set for photodegradation. Upon further studies of RB in THF spiked with 4 wt.% PMMA, where kinetics would show the furthest evolution in fading, RB is seen to degrade similarly to the PS and PVC spiked solutions (see Figure 17).

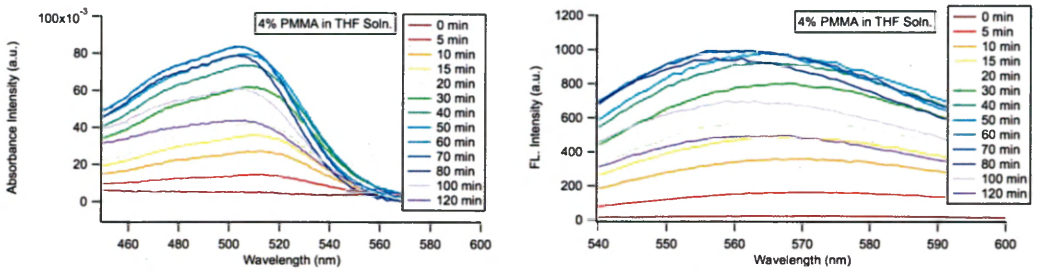

Figure 17: Absorbance and Fluorescence of RB-THF solution in 4 wt.% PMMA

Recalling the previous section, Group 3 behavior is defined by RB degradation with a minor (≤10 nm) blue shift within the ethyl acetate solvent. Group 3 behavior was abandoned when PS was added to RB in ethyl acetate solutions (see Figure 18). A rising baseline as irradiation time increases suggests insolubility, and the blue shift of over 15 nm reveals a change of behavior of RB, somewhere between group 2 and 3. This shift in behavior either brings to light the increasing reactivity of RB leading to N-dealkylation of the diethylamino substituents with more irradiation time, or simply reveals a solubility issue. In comparison, when RB in ethyl acetate was spiked with 12 wt.% PMMA, minor blue shift behavior of group 3 was maintained.

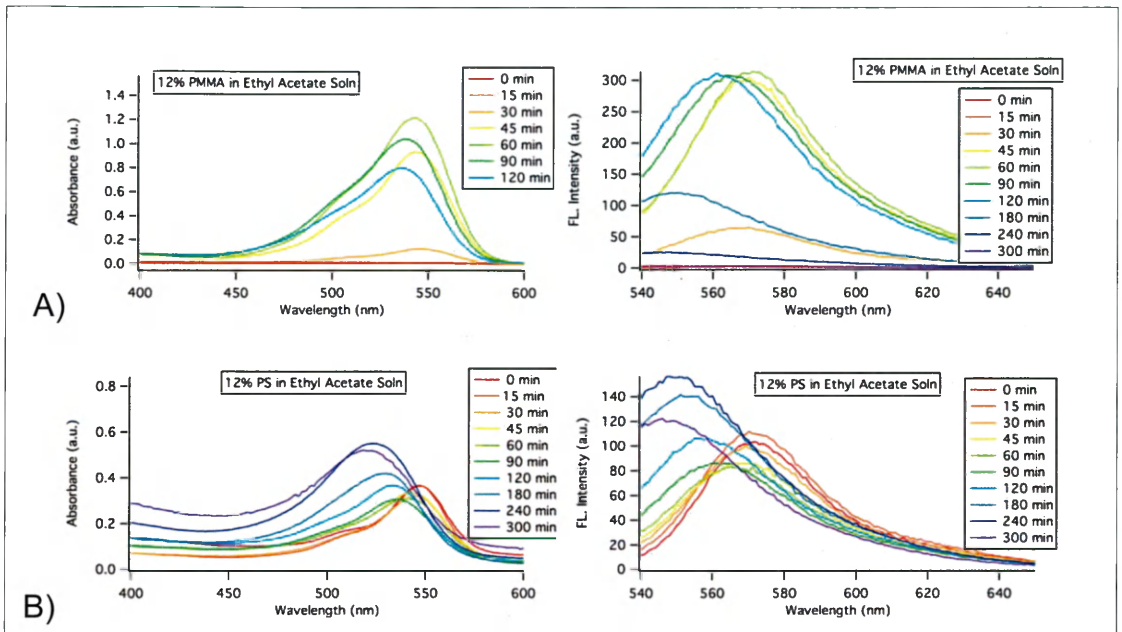

Figure 18: Absorbance and Fluorescence of RB-Ethyl Acetate soln. with 12 wt.% Polymers: A) PMMA B) PS

When polymers are in solution with RB, the solvent plays a more major role in RB degradation classification than the polymer. The increasing polymer concentration in solution slows down the RB degradation kinetics by reducing the blue shift magnitude. With the addition of another oxidizable species to the solutions, the UV fading of RB also is reduced, since the singlet oxygen can now also interact with the polymer. However, with increasing irradiation time, issues of solubility limit the extent of analysis possible.

3.1.3 RB IN FILMS DATA

In order to solve the issue of decreasing solubility of polymers with increasing irradiation time, and to study RB in a solid environment more similar to that of a modern art plastic sculpture, the next phase of the project

involved casting films. Films were spin coated from the same solutions that were studied in the previous section. After initial comparison of RB fading within varying weight percent of each polymer film, there were two main observations: 1) the shape of the fluorescence spectrum of RB-fading within each polymer of varying concentrations is the same except for intensity differences, and 2) the behavior varies from one polymer to another. Unlike previous graphs, Figure 19 depicts the fluorescence intensity corresponding to λ_{max} of polymers at various wt.% and at increasing irradiation time.

In Figure 18, two groups of fluorescence behavior emerged. PC and PMMA films cast from RB-THF solutions demonstrated an initial increase and minor degradation as a function of time. In contrast, PS and PVC films cast from RB-THF solutions displayed fluorescence intensity with a steady decline.

The weight of polymer to weight of solution from which it was cast to make films was not varied in subsequent film experiments, due to initial AFM measurements indicating that the wt.% of polymer in solution translates to a change in thickness of the film, and varies from one polymer type to another. Unlike the data of RB in solvents or solutions with polymers where absorbance data proved useful to elucidate dye-polymer phenomena, the films did not give accurate or reproducible absorbance measurements.

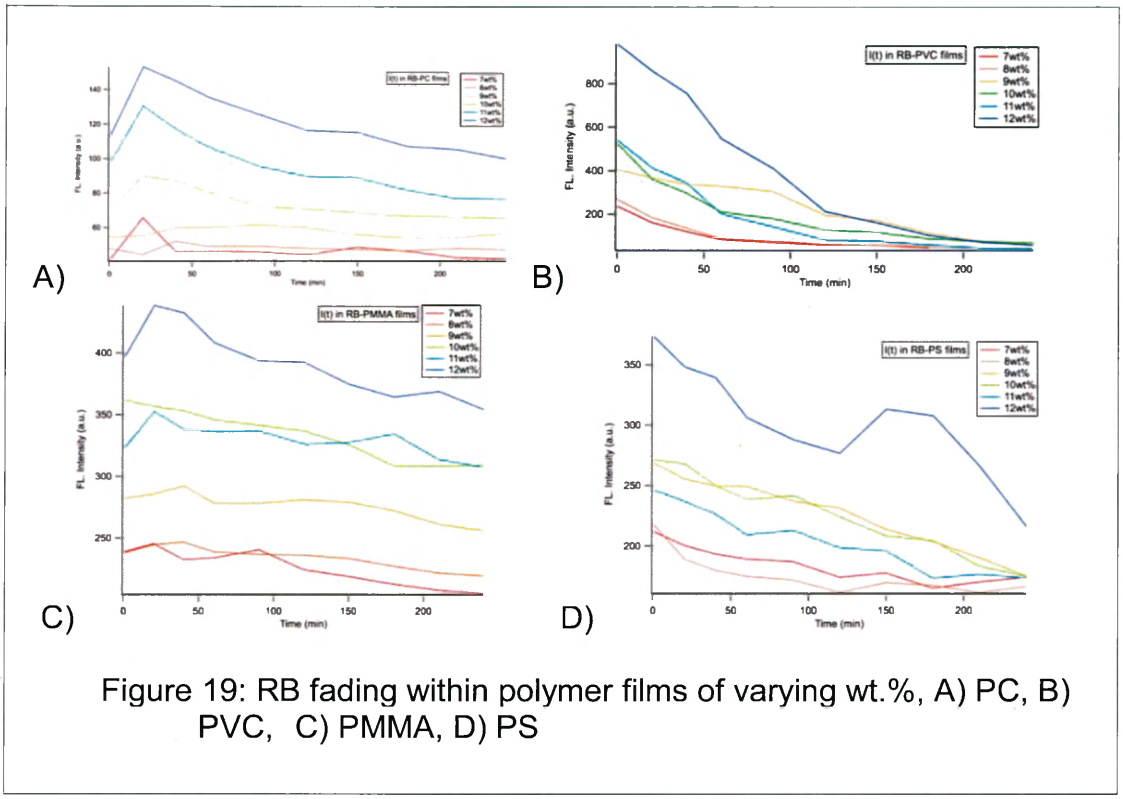

Figure 19: RB fading within polymer films of varying wt.%, A) PC, B) PVC, C) PMMA, D) PS

In order to understand the difference between the two types of trends of RB in polymer films, significant data were collected of films cast from as many solvents as the 12 wt.% polymer was soluble. If looking at Tables 11-14 while ignoring the unannealed data for the time being, a few trends emerge. The annealed polymer-solvent films do not show any wavelength shifting during RB fading, suggesting very protected RB molecules embedded in the films that have not yet undergone significant degradation leading to shifts.

Another trend within the quantitative data is that RB in PVC annealed films cast from acetic acid, ethyl acetate, and THF have the largest

fluorescence ΔI values, indicating the least stable polymer substrate of the films. Within the PVC combinations, the fluorescence ΔI value for a film cast from THF is 18.7 %, while the film cast from ethyl acetate is only 7.5 % (see Table 14). To recall the solution data set from the previous section, when RB in a THF solution with polymers was degraded, the fluorescence ΔI values showed a more pronounced stability compared to RB-polymer solutions within chloroform or ethyl acetate. This contrasting behavior in films compared to solutions shows the importance of the medium on the RB aging behavior. A film cast from the same solvent and polymer solution does not translate to identical RB fading; however, there seems to be a consistency within each medium.

For example, when comparing the fluorescence ΔI value of RB in a PS film cast from THF in Table 13, a value of 11.4% clearly distinguishes it from PS films cast from chloroform and ethyl acetate data of 2.7% and 1.6%. These data also reveal significant RB fading spectra in THF, reflecting group 2 fading of RB in PS and PVC within films cast from the same solvent. To support this interpretation, the data of RB-PC and RB-PMMA films cast from chloroform both have larger fluorescence ΔI values values than when cast from THF (see Tables 11 and 12).

Film Composition	Unannealed Films		Annealed Films	
	Fluorescence ΔI (%) up to 75 min	Δλ (max-min)	Fluorescence ΔI (%) up to 75 min	Δλ (max-min)
RB/PC in Chloroform	15.9 (increased)	-	5.1	-
RB/PC in THF	11.8	-	0.55	-

Table 11: Quantitative Data for 12 wt.% PC films

Film Composition	Unannealed Films		Annealed Films	
	Fluorescence ΔI (%) up to 75 min	Δλ (max-min)	Fluorescence ΔI (%) up to 75 min	Δλ (max-min)
RB/PMMA in Acetonitrile	4.2	-	-	-
RB/PMMA in Chloroform	18.6	-	3.7	-
RB/PMMA in Ethyl Acetate	5.6	-	4.4	-
RB/PMMA in THF	2.5	-	0.23	-

Table 12: Quantitative Data for 12 wt.% PMMA films

Film Composition	Unannealed Films		Annealed Films	
	Fluorescence ΔI (%) up to 75 min	Δλ (max to min)	Fluorescence ΔI (%) up to 75 min	Δλ (max to min)
RB/PS in Chloroform	2.5	565 nm → 570nm in 45min (5 nm)	2.7	-
RB/PS in Ethyl Acetate	4.2	-	1.6	-
RB/PS in THF	8.4	-	11.4	-

Table 13: Quantitative Data for 12 wt.% PS films

Film Composition	Unannealed Films		Annealed Films	
	Fluorescence ΔI (%) up to 75 min	Δλ (max-min)	Fluorescence ΔI (%) up to 75 min	Δλ (max-min)
RB/PVC in Acetic Acid annealed	-	-	19.2	-
RB/PVC in Ethyl Acetate	58.5	572.05 nm → 561.94 nm in 45 min (~10 nm)	7.5	-
RB/PVC in THF	56.0	572.95 nm → 565.07 nm (7 nm)	18.7	-

Table 14: Quantitative Data for 12 wt.% PVC films

In solutions, the solvent identity had the most significant influence on RB fading behavior. In contrast, the casting solvents in films seem to have minimal influence in comparison to the polymer identity for classification of behavior. In order to find a mode between the solution and solid film data, the medium was changed to an unannealed film. In these types of films, there is a lack of equilibrium, due to the molecules ending up wherever spin coating randomly places them.

First glance of the quantitative comparisons of RB degradation in unannealed versus annealed polymer films shows a trend in $\Delta\lambda$ values between the maximum and minimum spectra within the first 75 minutes of UV degradation. Supporting the conclusion that polymer films of PS and PVC fade RB more drastically than PC and PMMA, these data show that RB in PS and PVC films also undergo a $\Delta\lambda$ shift in fluorescence. Within the first section of the discussion, this $\Delta\lambda$ shift in fluorescence of RB in solvents was interpreted as the increased exposure of RB to oxygen molecules, thus accelerating photo-oxidation, including the mechanism for N-deethylation of the diamine groups.

The film qualitative spectra show the pronounced blue shift in PVC, but a minor red shift in PS, revealing a new type of behavior in these data. In Figure 20, the fluorescence spectrum of unannealed PS film cast from a RB-THF solution shows an initial decrease. This abnormal data set is not reflective of RB degradation, but is the influence from the excitation

wavelength onto the fluorescence spectrum. Looking closely at the spectrum of the red shift in the unannealed film cast of PS in RB-THF solution, there are jagged lines of the initial spectra on the unannealed film, and the shift is not beyond, but only up to 570 nm. This initial spectrum therefore, seems to be a poor data point that is not significant to the results interpretation.

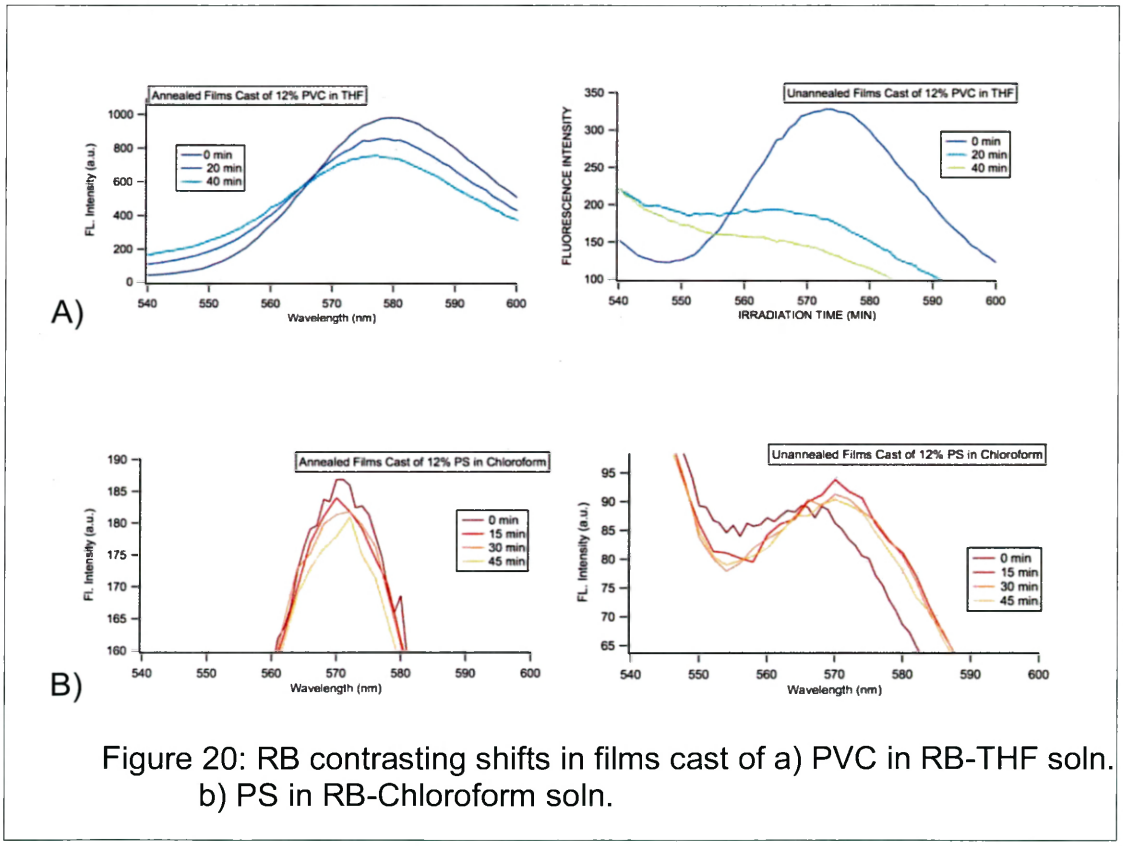

Figure 20: RB contrasting shifts in films cast of a) PVC in RB-THF soln. b) PS in RB-Chloroform soln.

Looking back to the quantitative summary in Tables 11-14, a comparison between the unannealed and annealed fluorescence ΔI values can be made. Using the quantitative data of the fluorescence of RB, an average was calculated of the ratio of unannealed films ΔI values: annealed

films ΔI values in solvents ethyl acetate or THF. In a RB-PMMA film cast from the solvents ethyl acetate or THF, the ratio was 7.5, in PVC 5.4, and in PS 1.68, suggesting that across all polymers the RB degradation in unannealed films cast from either ethyl acetate or THF display larger fluorescence changes representing RB fading than in annealed films. One interpretation of the behavior in annealed films being more stable compared to unannealed films is that the process of annealing de-oxylated the films. Another possible interpretation involves questioning how the polymer physical structure may be hindering or accelerating degradation of RB molecules in annealed versus unannealed films.

To continue to utilize the fluorimeter to probe the reasoning behind behavior in unannealed compared to annealed films, the project used fluorescence anisotropy. Fluorescence anisotropy is used as a means to measure molecular motion. The origin of anisotropy comes from the measurement of transition moments for absorption and emission along specific directions of the fluorophore structure.[52] Possible causes of depolarization of emission include rotational diffusion and angular displacement of the fluorophore; where the latter relies on rate and extent of diffusion during the excited state lifetime, and can be attributed to viscosity of the solvent, size, and shape of the rotating molecule.[52] Fluorescence anisotropy values (r) approaching 1 indicate completely polarized emission

due to less to no mobility, and values further from 1 mean depolarized emission due to more mobility.

In order to test if unannealed films give RB more mobility than annealed films, PVC films were cast from RB solutions of ethyl acetate and THF. PVC films were used instead of films made from another polymer due to RB having the largest ΔI-values in PVC than the other films. It was hoped that with more pronounced degradation, there would be a greater likelihood of observing a change in anisotropy values upon using annealed films of RB and PVC.

While probing the anisotropy of bulk RB molecules during their UV degradation within the annealed compared to unannealed films of PVC, trends brought to light some conclusions. In both graphs in Figure 21 of anisotropy values as a function of irradiation time, annealed films show an increasing polarization of RB emission, while unannealed films reveal a decreasing polarization, and thus depolarization of RB molecules as a function of degradation time. The anisotropic trends are the same in both graphs, suggesting the insignificance of the solvent from which the film was cast for these values.

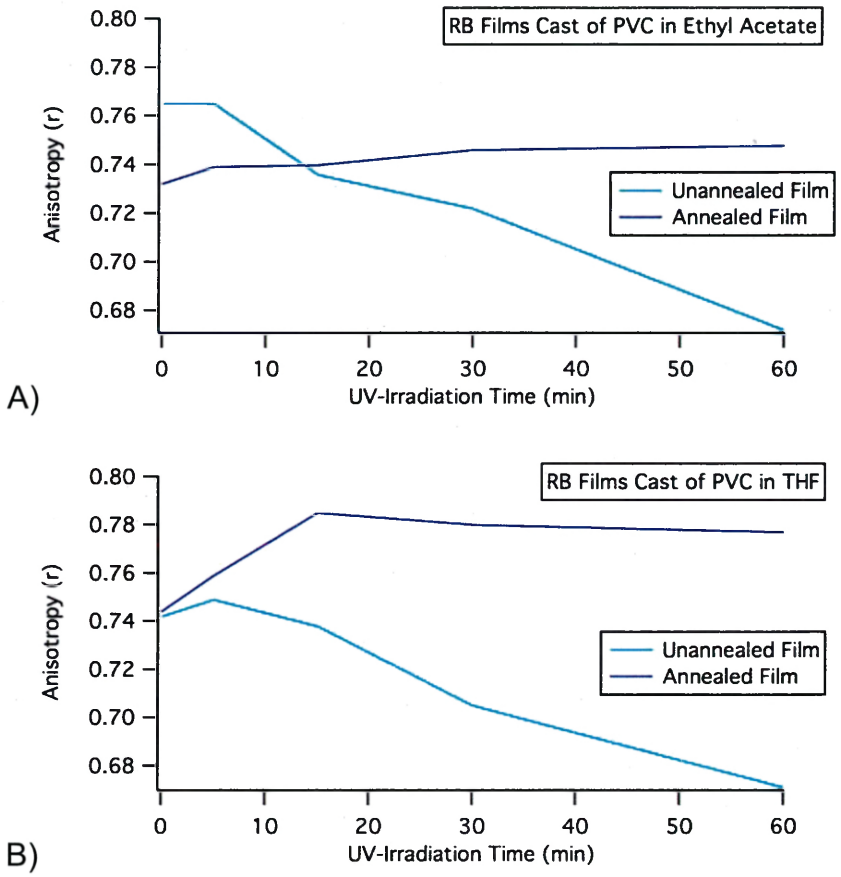

Figure 21: Fluorescence Anisotropy Data of RB-Fading in PVC films: A) Cast in Ethyl Acetate B) Cast in THF

The RB data within unannealed polymer films show increasing mobility of RB molecules with increasing interaction with polymer molecules. However, the RB data within polymer solutions reveal that with increasing polymer concentration the slower the speed of RB degradation. It is interesting to observe that there was increased access to the polymer surface

area in unannealed films, which undergo more degradation than annealed films. Therefore, the medium surrounding RB proves imperative for the prediction of RB fading behavior.

In the case of the solvent for casting, no trends could be found in the film data. When comparing the RB fading in a solution of THF, to a solution of 12 wt.% PS in THF, to a film cast of 12 wt.% PS in THF, data illustrate major conclusions about each medium (see Figure 22). The amount of time it took for RB to completely degrade in the film compared to the solvent without polymer, a difference of ~1000 min is evident. Comparing the RB-solvent data to the RB-solution data with the presence of the polymer reveal similar kinetics, with a blue shift affected by the polymer presence. These data reveal that the addition of another oxidative species like these polymer molecules to a solution shields RB molecules from fading and wavelength shifting. When RB and polymer molecules are cast into a film, wavelength shifts and dye degradation show significantly slower kinetics. These data reveal that RB molecular species are maintained longer within films, as well as a preservation of RB absorbance wavelength. Film media, especially cast from solutions with THF demonstrate superior RB lightfastness.

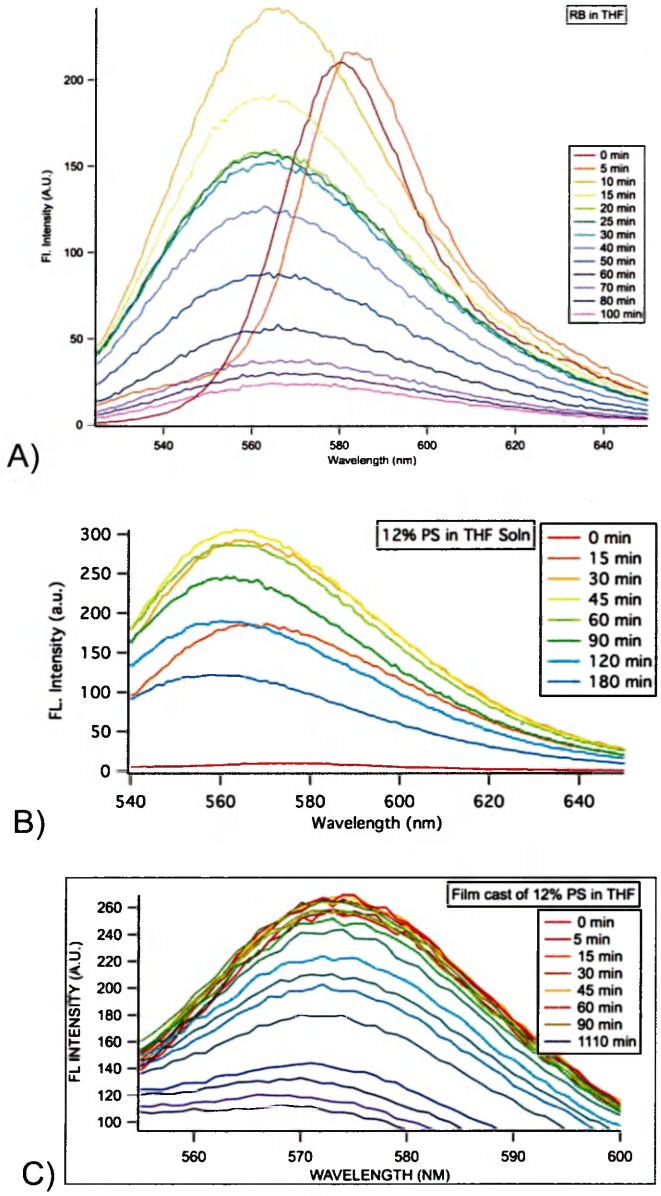

Figure 22: Complete Fading Films compared to Solutions: A) RB in THF, B) RB & 12 wt.% PS in THF, and C) RB film cast of 12 wt.% PS in THF

CHAPTER 4. CONCLUSIONS

Data of RB fading in solvents, solutions with polymers, and films demonstrate the importance of blocking oxygen from interaction with an RB molecule during its interaction with UV light for preservation of its colorant properties. Possible future work from this project would be to probe the polymers' degradation during the RB photo-fading process through IR and ESR studies. Further, studies of RB in solvents would be monitored with IR to elucidate vibrational interactions with oxygen. Other important future work would include degassing solvents and comparing the RB fading behavior, as well as using Thermal Gravimetric Analysis (TGA) to confirm the solvents in unannealed films have evaporated.

The consequences of this work include the increased fluorescence intensity over time of RB in film form over solution form, which is significant for laser applications where solution lasers are currently used. In solutions, the solvent identity had the most significant influence on RB fading behavior, however, the casting solvents in films seem to have minimal influence in comparison to the polymer identity for classification of behavior.

For the application to the conservation of art made of these materials, a conservator can learn from this study. In the context of Adams' mechanism and for the prevention of quenching RB, it is important not to surround the RB molecule with other oxidizable materials during treatments. The immediate environment and the ability for oxygen to penetrate through the medium to the

dye is of upmost importance no matter what phase is being studied. This author suggests using non-oxidizable solvents with RB, such as those containing nitrogen atoms, or act as acids or bases. If necessary to surround an RB dye molecule with a polymer species, one that produces fewer radicals in its own degradation, such as PC is more advisable than PVC. When making films or solids with RB dyes, it is imperative to stabilize the substrate with the annealing process in order to reduce reactivity, mobility, and non-radiative pathways to quench the fluorescence colorant. In the case of plastic art dyed with fluorescent RB molecules, conservation solutions must be developed in order to protect these solids from the oxygenated environment of a museum; however, thankfully no art is yet known of these materials in solution form.

WORKS CITED

1.Hinde, E.; Nel, P.; Slogget, R.; Roberts, A.; Fluorimetric Analysis of the Constituent Dyes within Daylight Fluorescent Pigments: Implications for Display and Preservation of Daylight Fluorescent Artwork, *Journal of the American Institute for Conservation* **2013**, *52*, 2, 97-106.

2. Shashoua. Y.;*Conservation of Plastics: Materials science, degradation and preservation*, Elsevier Ltd.: Oxford, 2008.

3. Vickerstaff, T.; II.Scientific Aspects, *Journal of the Royal Society of Arts* **1964**, *112*, 5091, 153-166.

4. Karstens, T.; Kobs, K.; Rhodamine B and Rhodamine 101 as Reference Substances for Fluorescence Quantum Yield Measurements, *J. Phys. Chem.* **1980**, *84*, 1871-1872.

5. Evans, N.A., Stapleton, I.W., Chapter VI- Structural Factors Affecting the Lightfastness of Dyed Fibers. In *The Chemistry of Synthetic Dyes* 8th ed.; Academic Press: New York, 1978, 221-277.

6. Giles, C.H.; Johari, D.P.; Shah, C.D.; Some Observations on the Kinetics of Dye Fading, *Textile Research Journal* **1968**, *38*, 1048-1056.

7. Lopez-Arbeloa, F.; On the Aggregation of Rhodamine B in Ethanol, *Chem. Phys. Letters* **1988**, *148*, 253- 258.

8. Korobov, V.E.; Triplet State of Rhodamine Dyes and its Role in Production of Intermediates, *Chem. Phys. Letters* **1977**, 45, 498-501.

9. Adams, D.; Lifetime of singlet oxygen in liquid solution, *J. Chem. Society: Faraday transactions II* **1972**, *68*, 4, 586- 593.

10. Meier, H. Chapter VII- Photochemistry of Dyes. In *The Chemistry of Synthetic Dyes*, 4th ed.; Academic Press: New York, 1971, 389-514.

11. Lopez-Arbeloa, I.; Ruiz-Ojeda, P.; Molecular Forms of Rhodamine B, *Chemical Physics Letters* **1981**, *79*, 347-350.

12. Evans, N.A.; Photofading of Rhodamine Dyes I- Identification of some Rhodamine B Photoproducts, *J. of the Society of Dryers and Colourists* **1970**, *86*, 174- 177.

13. Evans, N.A.; Photofading of Rhodamine Dyes II- Photode-alkylation of Rhodamine B, *J. of the Society of Dryers and Colourists* **1973**, *89*, 332.

14. Evans, N.A.; Photofading of Rhodamine Dyes III- The Effect of Wavelength on the Fading of Rhodamine B, *Textile Research Journal* **1973**, *43*, 697-700.

15. Oster, G.; Bellin, J.S.; Photoreduction of Triphenylmethane Dyes in the Bound State, *Journal of?* **1956,** *78*, 294- 298.

16. Broyde, B.; Oster, G.; Photoreduction of Dyes in Rigid Media II- Photoredux Properties of Thiazine Dyes, *J. of?* **1959**, *81*, 5099-5103.

17. Egerton, G.S.; Morgan, A.G.; The Photochemistry of Dyes I: Fundamental Principles, *J. of Society of Dyers and Colourists* **1970**, *86*, 79-83.

18. Foote, C.S.; Photosensitized Oxygenations and the Role of Singlet Oxygen, *J of?* **1967**, *1*, 104- 110.

19. Chibisov, A.K.; Kezle, H.A.; Levshin, L.V.; Slavnova, T.D.; Unimolecular Decay of the Excited States of Rhodmine Dyes, *J. Chem. Society: Chem. Comm.* **1972**, *23*, 1292-1293.

20. Wantanbe, T.; Takizawa, T.; Honda, K.; Photocatalysis through Excitation of Adsorbates. 1. Highly Efficient N-Deethylation of Rhodamine B Adsorbed to CdS, *J. Phy. Chem.* **1977**, *81*, 1845-1851.

21. Cumming, J.; Photochemistry of dyes on proteins and other substrates, *Journal of the Society of Dyers and Colourists* **1956**, *72*, 8, 373-381.

22. Bentley, P.; McKellar, J.F.; Phillips, G.O.; The Photochemistry of Dyes, Fibres, and Dye-Fibre Systems, *Review of Progress in Coloration and Related Topics* **1974**, *5*, 33-48.

23. McLaren, K.; The Action of Light on Colouring Matters, *J. Soc. Cosmetic Chemists* **1967**, *18*, 245-264.

24. Moura, J.C.V.P.; Oliveira-Campos, A.M.F.; Griffiths, J.; The Effect of Additives on the Photostability of Dyed Polymers, *J. Dyes and Pigments* **1997**, *33*, 173-196.

25. Giles, C.H.; Duff, D.G.; Sinclair, R.S.; The Relationship Between Dye Structure and Fastness Properties, *Review of Progress in Coloration and Related Topics* **1982**, *12*, 58-65.

26. Lewis, G.N.; Lipkin, D.; Reversible Photochemical Processes in Rigid Media: The Dissociation of Organic Molecules into Radicals and Ions, *J. of ?* **1942**, *64*, 2801- 2808.

27. Faucitano, A.; Buttafava, A.; Camino, G.; Greci, L.; Photo-oxidation and stabilization of polymers, *Trends in Polymer Science* **1996**, *4*, 92-98.

28. Chabira, S.F.; Sebaa, M.; Huchon, R.; De Jeso, B.; The changing anisotropy character of weathered low-density polyethylene films recognized by quasi-static and ultrasonic mechanical testing, *Polymer Degradation and Stability* **2006**, *9*, 1887-1895.

29. Binns, M.R.; Lukey, C.A.; Hill, D.J.T.; O'Donnell, J.H.; Pomery, P.J.; A New Technique for the Study of Reactive Species Generated During the Initial Stages of Polymer Photodegradation, *Polymer Bulletin* **1992**, *27*, 421-424.

30. Rabek, J.F.; Chpt. 4: Photo-oxidative Degradation. In Photodegradation of Polymers; *Physical Characteristics and Applications*; Springer: New York, 1996, 51-97.

31. Blank, S.; An Introduction to Plastics and Rubbers in Collections, *Studies in Conservation* **1990**, *35,* 2, 53-63.

32. Brydson, J.A. *Plastic Materials,* 7^{th} ed.; Butterworth-Heinemann: Boston, 1999.Romani

33. Pickett, J.E. Reversible Post-Exposure Yellowing of Weathered Polymers. In *Polymer Degradation and Stability* **2004**, *85*, 681-687.

34. Moadhen, A.; Elhouichet, H.; Oueslati, M.; Stokes and anti-Stokes Photoluminescence of Rhodamine B in Porous Silicon, *Materials Science and Engineering C* **2002**, *21*, 297-301.

35. McNeil, I.C. Fundamental Aspects of Polymer Degradation, In *Polymers in Conservation*; Allen, N.S., Edge, M., Horie, C.V., Eds. Royal Society of Chemistry: Cambridge, 1992.

36. Zweig, A.; Henderson, W.A.; Singlet Oxygen and Polymer Photooxidations I: Sensitizers, Quenchers, and Reactants, *J. Polymer Science, Polymer Chemistry Edition* **1975**, *13*, 717-736.

37. Alhamedi, F.H.; Rauf, M.A.; Ashraf, S.S.; Degradation Studies of Rhodamine B in the Presence of UV/ H_2O_2, *Desalination* **2009**, *239*,

159-166.

38. Dubois, A.; Canva, M.; Brun, A.; Chaput, F.; Boilot, J.P.; Enhanced Photostability of Dye Molecules Trapped in Solid Xerogel Matrices, *Synthetic Metals* **1996**, *81*, 305-308.

39. Lopez-Arbeloa, I.; Rohatgi-Mukherjee, K.K.; Solvent effects on photophysics of the molecular forms of rhodamine B. Solvation models and spectroscopic parameters, *Chemical Physics Letters* **1986**, *128*, 474-479.

40. Korobov, V.E.; Shubin, V.V.; Chibisov, A.K.; Triplet State of Rhodamine Dyes and its Role in Production of Intermediates, *Chem. Phys. Letters* **1977**, *45*, 498- 501.

41. Signma-Aldrich guide (web based)

42. Allen, N.S.; Photofading of Basic Triphenylmethane Dyes: Evidence for Electron Tranfer, *Dyes and Pigments* **1981**, *2*, 31-35.

43. Mchedlov-Petrosyan, N.O.; Fedorov, L.A.; Sokolovskii, S.A.; Surov, Y.N.; Salinas-Maiorga, R.; Structural Conversions of Rhodamines in Solution, *Bulletin of the Russian Academy of Sciences, Division of Chemical Science* **1992**, *41*, 403-409.

44. Montalti, M; Credi, A.; Prodi, L.; and Gandolfi, M.T.; Handbook of Photochemistry, 3rd ed.; Taylor &Francis Group: New York, 2006.

45. Urrecha- Aguirresacona, I.; Lopez-Arbeloa, F.; Lopez-Arbeloa, I.; Spectroscopic and Thermodynamic Study on the Aggregation of Rhodamines in Solution, *J. Chemical Education* **1989**, *66*, 866-869.

46. Lopez-Arbeloa, I.; Ruiz-Ojeda, P.; Dimeric States of Rhodamine B, *Chemical Physics Letters* **1982**, *87*, 556-560.

47. Rohatgu- Mukherjee, K.K.; Lopez-Arbeloa, I.; Correlation of Liquid Structure with the Photophysics of Rhodamine B (acidic, basic and ester forms) in Water-Ethanol Mixed Solvent, *J. Photochem. Photobiol. A: Chem.* **1991**, *58*, 277-288.

48. Lopez-Arbeloa, T. Lopez-Arbeloa, F.; Hernandez-Bartolome, P.; Lopez-Arbeloa, I.; On the Mechanism of Radiationless Deactivation of Rhodamines, *J. Chemical Physics* **1992**, *160*, 123-130.

49. Merkel, P.B.; Kearns, D.R.; Radiationless Decay of Singlet Molecular Oxygen in Solution: An Experimental and Theoretical Study of Electronic- to- Vibrational Energy Transfer, *J. Am. Chem. Soc.* **1972**, *94*, 7244-7253.

50. Lopez-Arbeloa, F.; Lopez-Arbeloa, T.; Tapia-Estevez, M.J.; Lopez-Arbeloa, I.; Photophyics of Rhodamines- Molecular Structure and Solvent Effects, *J. Phys. Chem.* **1991**, *95*, 2203-2208.

51. Kearns, D.R. Chapter 4: Solvent and Solvent Isotope Effects on the Lifetime of Singlet Oxygen. In *Organic Chemistry*, Academic Press: New York, 1979, 115-136.

52. Lakowicz, J.R. *Principles of Fluorescence Spectroscopy*, 2nd ed.; Kluwer Academic/Plenum Publishers: New York, 1999.